MERCURY AT THE BERRY'S CREEK SITE
BERGEN COUNTY, NEW JERSEY:
An Evaluation of Potential Hazards Created by Dredging

Submitted to:

VENTRON DIVISION

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SUMMARY

Numerous monitoring activities in the vicinity of the dismantled mercury processing plant near Berry's Creek, Bergen County, New Jersey, have determined that significant levels of mercury exist in the site vicinity. Most of the mercury is currently bound to site soils and the sediment in Berry's Creek and the adjacent marsh. A number of field and laboratory programs have been carried out by various investigators to determine the extent of mercury migration out of Berry's Creek, the level of contamination in the food chain, and the existence or extent of any health hazard posed to the community. To date, these analyses have confirmed the presence of mercury in the creek sediments and site soils, but have failed to reveal any significant movement of mercury from the sediments or any health and toxicity effects. A description of the various monitoring programs and the results from the site investigations are summarized in this report.

The State of New Jersey proposes to dredge Berry's Creek in order to remove the mercury contaminated sediments. Disposal of the sediment would occur in a diked portion of the 33 acre tract adjacent to the mercury plant site. It would appear that the State has concluded that, although the mercury is not currently a health hazard, conditions may change such that a hazard may occur. Some technical experts contend, however, that the dredging itself will mobilize the mercury which is stable under current conditions, thereby creating the hazard sought to be avoided. These experts cite the long-term stability of the mercury which was deposited in the mid-19th century in San Francisco Bay sediments (Wood, 1980).

A geochemical model of the various forms of mercury under current and dredged conditions was conducted as part of this study. It was found that mixing the mercury contaminated sediments

IT would also remove The mercury!

with Berry's Creek water may substantially increase the level of mercury in solution. The increased solubility would result in greater dispersion of the mercury and may act to increase the rate of conversion of inorganic forms of mercury to the more toxic organic forms (methyl-mercury). It is also possible that the high levels of mercury and other metals in the sediment currently prevent the growth of bacteria which convert mercury to its more toxic forms. If this is the case, then dredging of the highly contaminated sediment may remove the bacterial inhibition, allowing more efficient conversion to the more toxic methyl-mercury form. Details of the geochemical model analysis are presented in this report.

? dredging

In summary, it is our opinion based on results of the geochemistry model and other mercury studies at Berry's Creek that:

- the current conditions at the site are stable with respect to mercury mobility
- dredging of sediments containing mercury may create a more detrimental environmental problem than leaving the mercury in its present stable condition
- there is no evidence for toxic effects to biota, or adverse health effects at or near the site

dredging site, disp site or both?

Since dredging may disturb the apparent current stability, we recommend that this matter be evaluated further prior to undertaking any dredging, and that alternative measures designed to maintain or enhance mercury stability be investigated.

INTRODUCTION

The Berry's Creek site in Bergen County, New Jersey has been the focus of litigation concerning the removal of mercury contaminated sediment resulting from the operation of a mercury processing plant at the site. This plant operated from about 1930 to 1974 under the ownership of several companies. Discharge of mercury-laden effluent to Berry's Creek and possible spills on the site have resulted in significant levels of mercury in the site soils and channel sediments. Previous owners of the property are currently under court order to finance some part of remedial measures related to mercury in the sediment and soils. New Jersey devised a dredging plan for the Creek and obtained court approval to at least submit this plan to the Corps of Engineers. A dredging permit and an evaluation of the environmental impacts of the plan will be required from the Corps of Engineers prior to implementation.

This study was undertaken by Woodward-Clyde Consultants (WCC) at the request of Ventron to evaluate the numerous monitoring programs conducted by others in the vicinity of the site, and the possible effects of dredging on the apparently stable condition of mercury in Berry's Creek. Thus, the scope of this study was limited to an evaluation of available geochemical data by performing a model study on the effects of dredging at the site. Additional site investigations and monitoring were not included in the scope of the project. Data were available from previous site monitoring programs and a site visit were used to develop the assumptions used in the geochemical model.

This report is organized to provide a description of the site geology and hydrogeology, a summary of the monitoring programs conducted by others, and the results of the geochemical modeling

study conducted by WCC. An appendix provides information on the assumptions used in the model, model documentation, and the results from additional cases tested.

REGIONAL GEOLOGY

The Berry's Creek Site, an area of fill located in the Berry's Creek tidal marsh, is located in the watershed of the Hackensack River which is underlain by bedrock of the Late Triassic Age, namely, the Newark group of sedimentary rocks. The Brunswick Formation, a member of the Newark group, forms the surficial bedrock of the area. Bedrock is overlain by glacial deposits, lake deposits, and Recent alluvium.

The Newark group consists of non-marine sedimentary rocks which were deposited by streams or in lakes. Volcanism at the time formed thick lava flows which today form the Watchung Mountains west of Hackensack Meadowlands. A later episode of igneous intrusion today is preserved as the Palisades, a prominent escarpment located on the west side of the Hudson River, which forms the ridge east of the Hackensack Meadowlands.

After deposition of the Triassic sediments and the igneous activity, the rocks were faulted and tilted such that they now dip 15 to 20 degrees toward the northwest. Subsequent erosion was responsible for the basic topography of the area as it exists today. The sediments, particularly the red shale of the Brunswick Formation, eroded relatively rapidly, whereas, the rocks that formed the Watchung Mountains and the Palisades are more resistant and, therefore, form the prominent ridges east and west of the Hackensack Meadowlands. As a result, the area of the Hackensack Meadowlands was eroded to form a broad valley.

During the Pleistocene Epoch, at least three ice sheets advanced from the north and covered the northern part of New Jersey. The most recent ice sheet, the Wisconsin, moved as far south as Long Island, Staten Island and Perth Amboy and covered the entire Hackensack River basin. During the advance of the ice sheet, the ice further eroded the Hackensack Meadowlands area. When the advanced stopped or slowed, material in the ice was deposited and today is called till or moraine. In this area the till is red or brownish-red in color, and it is composed largely of particles of the nearby bedrock, the Brunswick Shale.

In the area of Berry's Creek, the till ranges in thickness from one to ten feet. Further to the south, the moraine is thicker and formed a dam across the lower section of Newark Bay. As the ice melted, the dam formed an impoundment in the area of the Hackensack Meadowlands called Glacial Lake Hackensack. Melt waters entering the lake carried sediments and deposited fine-grained sediments on the lake bottom. The lake functioned as a settling pond for these finer grained sediments for a period of about 2500 years, during which time up to 200 feet of fine-grained lake bottom sediments were deposited.

The dam that was formed by the moraine of the Wisconsin ice sheet was breached about ten thousand years ago and Glacial Lake Hackensack drained to the sea. Since then, the area has remained as a level wetland and is now known as the Hackensack Meadowlands. The remains of wetland vegetation, in mixture with mineral sediments, form deposits of material that are known as peat or meadowmat. The peat or meadowmat now form a thin surficial layer over much of the Hackensack Meadowlands district and range in thickness from four to twenty feet.

In summary, the geology of the vicinity of Berry's Creek tidal marsh consists of a surficial layer of meadowmat over which

fill material was placed at the Berry's Creek property. An unknown thickness of varved clays, silts and fine sands deposited in Glacial Lake Hackensack and till deposited by the Wisconsin ice sheet occurs below the site. The bedrock is estimated to be at a depth of more than 50 feet at the site.

SITE GEOLOGY AND HYDROGEOLOGY

Information on the detailed geology at the site is limited to a report by Hutchinson (undated, NJDEP). In 1977, seven monitoring wells were installed at the site in addition to the two wells previously drilled. The monitoring wells were installed under the supervision of, and logged by, personnel of New Jersey Department of Environmental Protection (NJDEP), who surveyed the elevation of the wells and measured the water tables. The locations of these wells, ranging in total depth from 10 to 24 feet, are depicted in Figure 1. At each of the boring locations, fill occurred from the surface to a depth of 3.5 to 18 feet (Boring W-2). The fill was underlain by peat, silt, clay, or sand beds. Sand layers were identified in each of the borings, except for Borings W-2 and W-6.

During drilling, the water table was encountered within or above the sand beds identified in the boring logs, at depths of three to seven feet below ground surface. Subsequent, stabilized water level measurements indicate the water table to exist at shallow depths (less than 2 feet below the surface) within the sand or fill material. The measurements were made for periods up to 10 hours to check both variation as tides changed and the areal distribution of hydraulic gradients at the site.

On each of the four occasions during June and July, 1977, the highest elevation of water was measured in Well No. 2. Lower elevations of water occurred in the other wells and nearby

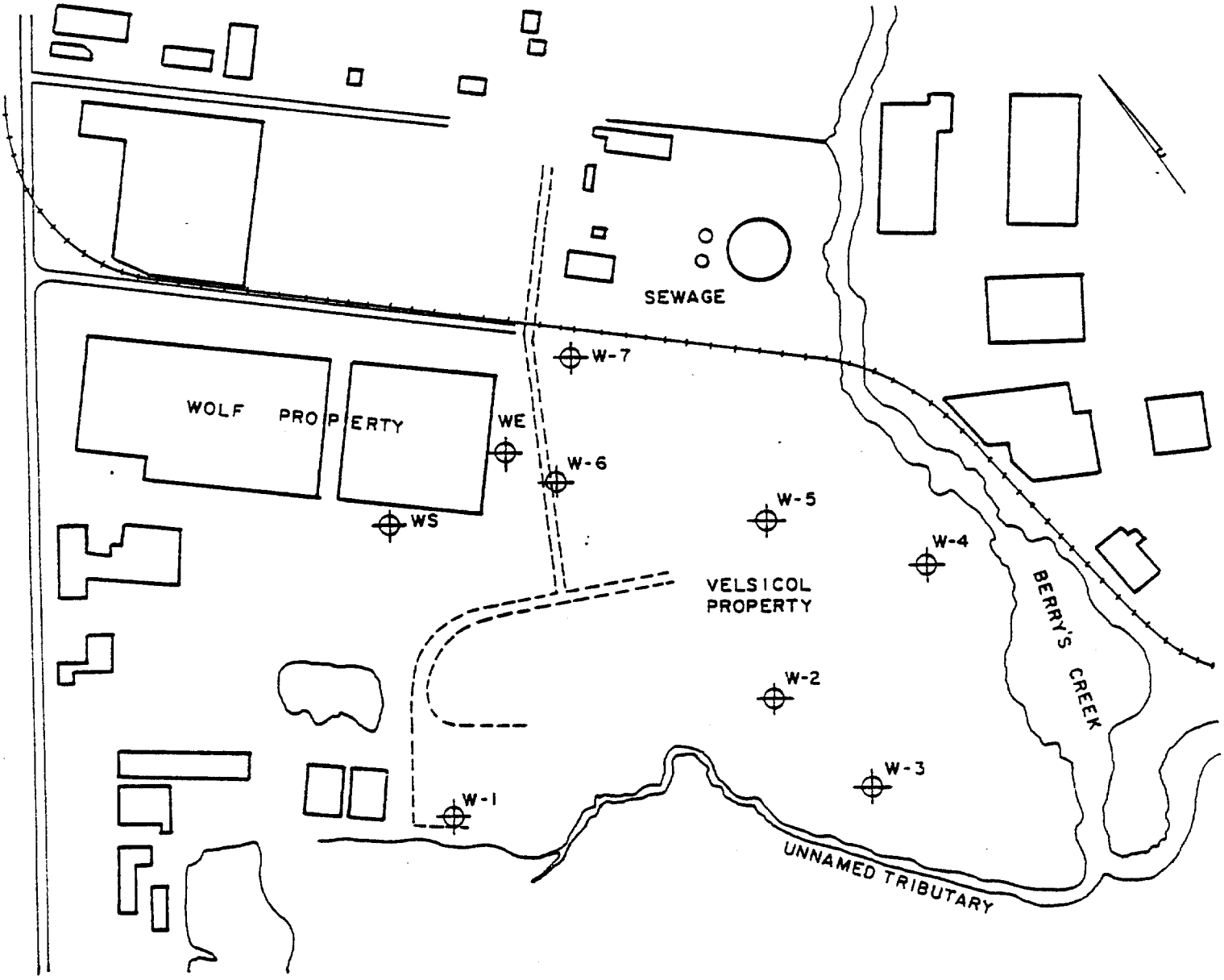

Fig. 1 LOCATION OF MONITORING WELLS

surface water. A groundwater gradient thus was established from the central part of the fill area (indicated as Velsicol Property on Fig. 1) toward Berry's Creek to the east and toward an unnamed tributary of Berry's Creek to the south. A drainage structure not shown on Fig. 1 is presumed to extend due east from the building denoted as Wolf Property (see Fig. 1) to the point of discharge at Berry's Creek. The lower elevations of the water measured in Well W-6 and Well WE suggest that the drainage structure serves as a line discharge. Thus, groundwater from the area of the fill also flows northeastward toward the drainage structure which is presumed to extend from the building to the discharge point.

On three occasions in July, 1977, NJDEP measured the water table elevations in the wells during a period that was approximately one-half tidal cycle (6 hours and 12 mins.). Data from these water level measurements indicate that the elevation of water in Wells W-6, WE and WS changed during the periods of measurement and was similar in direction to the change in tide that was measured in Berry's Creek. The response of Wells WE, WS, and W-6 suggest that the buried drainage structure from the Wolf property to the discharge responds freely with the tide in Berry's Creek. Other wells showed no response in water elevation that could be correlated to tidal changes in Berry's Creek.

Hydrologic data are insufficient to establish gradients, estimate transmissivities, or estimate the effective porosity of the material through which the uppermost groundwater flows. Thus, there can be no estimates made for the rate of flow or the seepage velocity of groundwater beneath the site and into Berry's Creek. The existing information indicates that precipitation infiltrates the fill area and flows at an unknown rate to Berry's Creek, the unnamed tributary of Berry's Creek located southwest of the Velsicol property, and northeastward toward the discharge pipe

that extends from the Wolf property to the discharge point at Berry's Creek.

SITE INVESTIGATIONS AND MONITORING OF MERCURY

The results of site investigations and monitoring performed by other investigators have been reviewed and are summarized below.

WATER QUALITY MONITORING

Initial monitoring at the site focused on the effluent composition during plant operation in terms of broad water quality parameters. The earliest mercury analyses available (October, 1970) showed 5 ppm in the unfiltered effluent and 1.6 ppm in the filtered effluent. On the basis of the unfiltered sample and assuming a 35 gpm discharge, a loading rate of 2.1 pounds per day to Berry's Creek was calculated. After treatment facilities were installed at the plant, the mercury concentration in the discharge was reduced to 0.40 pounds per day.

Analyses of groundwater and surface water (See Table 1) indicated different levels of mercury, depending upon whether the sample was filtered prior to analysis. Filtering removes the suspended materials which frequently adsorb large amounts of metals. In all cases where mercury was detected, the level was higher in the unfiltered samples, indicating the adsorption of mercury on very fine particles. This is corroborated by the observation that mercury concentrations are higher in the marsh sediments where water movement is slower and where fine particles may settle more easily than they do in the creek itself. Mercury in unfiltered samples was also higher during low tide when net water movement in the Creek was downstream, carrying particles away from the site.

EBB? Are they trying to say the greater current during ebb tide resuspend more sediments?

Who took samples? Need more info on this table. Location of sites. Do all data presented, or only selected data?

TABLE 1 - WATER QUALITY MONITORING PROGRAMS[1]

DATE	TYPE	FINDINGS
Mar. 1967	Effluent	High COD, BOD, color, turbidity, suspended solids, pH
Jan. 1969	Effluent	High COD, BOD, color, turbidity, suspended solids, nitrates; pH varied from 2.4 to 9.4
Oct. 1970	Effluent	Mercury in unfiltered effluent = 5 ppm; Hg in filtered effluent = 1.6 ppm
Oct. 1971	Effluent	Hg at final discharge = 0.970 ppm
Jan. 1972	Groundwater	Hg in filtered sample = 0.04 to 3.6 ppm; Hg in unfiltered sample = 5.5 to 2000 ppm
Jun. 1974	Surface water	Hg upstream of site = 0.0039 ppm; Hg downstream of site = 0.011 ppm
Aug. 1977	Groundwater	Hg in 8 of 10 wells <0.3 ppb; Maximum Hg = 8.8 ppb; water near warehouse = 67 ppb.
	Surface water	Hg and other metals measured over tidal cycle; maximum Hg concentration in unfiltered water = 88 ppm; mercury concentrations at low tide were higher, but only for unfiltered samples.
Fall 1978	Surface water	Hg in filtered samples <0.1 ppb; 9 samples <3.0 ppb Hg; one sample = 4 ppb; Maximum Hg in unfiltered samples=9.9 ppb; other areas in Meadowlands also sampled.
N/A	Surface water	Average Hg concentration for one month = 0.5 to 9.4 ppb in Berry's Creek; Hg in other areas of Meadowlands = 0.0 to 6.8 ppb

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[1]New Jersey Surface Water Standard: 5 ppb; Federal Drinking Water Standard: 2 ppb

N/A not available

The primary form of mercury in the filtered samples is considered to be dissolved mercury. It is this form which would be most likely to be transported beyond the Berry's Creek Basin. All filtered surface water samples contained less than 5 ppb mercury, which is the New Jersey standard for surface water. Similar levels were found in most of the filtered groundwater samples, though one sample had an 8.8 ppb mercury concentration. No information was available as to well construction or design, preventing evaluation of the reliability of such measurements.

SEDIMENT AND SOIL ANALYSIS

Analyses of site soils and sediment from the Berry's Creek channel and marsh indicate significant amounts of mercury contamination (See Table 2). Liquid mercury was observed in the top two feet of one soil core and can be inferred to exist in other samples based on high mercury concentrations observed (over 10% in some samples). The maximum mercury concentration occurred at the surface in some locations and at various depths in other samples. No descriptions of the samples were provided to allow correlation with the type of soil or depositional environment.

WCC personnel observed during a site visit that very distinct soil layers exist which should vary widely in the amount of mercury they would retain. Construction debris, undecomposed organic matter, and an unidentified white silty material occurred from the surface to a depth of approximately two to 20 inches. Below this, in the phragmites[1] area, was an extremely organic rich muck underlain by fine sandy material at a depth of approximately 48 inches. It would be expected that mercury would be strongly bound to the organic material and less so to the surface debris or underlying fine sand. Yeaple, et al (1972) observed a 10,000-fold difference in the fraction of soluble mercury between a sandy material and an organic peat. It is not known which of these layers

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[1] phragmites are a form of tall, plumed grass characteristic of this estuary

TABLE 2 - SEDIMENT AND SOIL ANALYSES[1]

DATE	INVESTIGATIONS/RESULTS
Aug. 1970	Sediment from upstream and downstream segments of Berry's Creek analyzed
N/A(1970?)	Mercury concentration in sediment at discharge pipe = 2825 ppm from 0-3" depth; maximum Hg (at 6-9" depth) = 89,162 ppm
Jan. 1972	WRCC/Ventron Study; 5-375 ppm Hg in soils
July 1974	Soil analyses near buildings; maximum Hg = 195,000 ppm; Hg droplets visable at surface and 1-2 ft. depth.
Sept. 1974	Hg in soils varied from less than 100 ppm to 142,500 ppm
Sept. 1976	Two surface sediment locations analyzed for total Hg, CH_3Hg^+ and volatile Hg
Aug. 1977	31 soil core samples; most contain less than 250 ppm Hg in cores, maximum Hg = 123,000 ppm; no consistent variations with depth; sediment samples from creek generally less than 1000 ppm; maximum Hg in sediment = 89,162 ppm.
Fall 1978	Monitoring over a one-year period; 42 locations throughout Meadowlands at 2" increments; Hg levels at Berry's Creek ranged from 0.1 to 2006 ppm in marsh soils; 0.1 to 1730 ppm in channel sediments; Hg in marsh greater than in channel sediment; Maximum Hg less than 160 ppm in sediment or marsh samples from outside Berry's Creek; no consistent relationship between Hg concentration and depth.
N/A	Sediment samples collected upstream and downstream of site on Berry's Creek; most of contamination within -400 to +3000 ft. of outfall.

N/A Not available.

[1] No standards applicable.

was sampled in the monitoring program, or if two or more units were combined in an effort to sample uniform depth intervals. This lack of information severely limits the interpretive value of the available soil chemical analysis data.

Marsh and channel sediments also contain substantial levels of mercury. The most heavily contaminated section occurs from 400 feet upstream to 3000 feet downstream of the outfall location. No consistent relationship between depth and concentration is apparent from the data. Concentrations may be a function of the nature of the sediment and/or the depositional environment, but that information is not provided in the report of the data. Marsh samples generally contained more mercury than channel sediments, possibly due to erosion in the channel, deposition of finer mercury-laden particles in the quieter marsh areas, or greater mercury adsorption onto organic rich marsh soils (Lindsay, 1979).

MERCURY LEVELS IN THE BIOTA

Extensive testing of mercury levels in the biota has been carried out in Berry's Creek and the Meadowlands by other investigators. Details of the studies are summarized in Table 3. In general, mercury levels are higher than normal throughout the Meadowlands (including Berry's Creek), but are less than the allowable maximum for edible portions of the fish and bird samples (1.0 ppm Hg). There does not appear to be any evidence that animals at Berry's Creek contain higher levels of mercury than at other areas of the Hackensack River. Mercury levels in the Berry's Creek vegetation are higher than in other areas, but no standard exists for plants. The conclusions drawn by Hackensack Meadowlands Development Commission (HMDC) personnel are that there is no evidence for toxic effects to biota at or near the site, but that further surveillance is warranted.

SOURCE?

Why are standards 1 ppm for consumption of fish & 2 ppb " drinking water?

Who took samples & analyzed data?

TABLE 3 - ANALYSES OF HG IN THE MEADOWLANDS BIOTA[1]

DATE	INVESTIGATIONS/RESULTS
Sept. 1976	Detectable levels of volatile mercury found in plants; level not specified
Feb 1977	Samples from Fall 1976: 8 of 14 fish samples exceeded 0.5 ppm; subsequent sampling failed to confirm high levels
1977 (DEP)	none of 18 fish, muscrat or pheasant samples exceeded 0.5 ppm Hg
1977 to 1978	(a) aquatic samples: one sample of fish muscle from Berry's Creek contained 1.877 ppm Hg; 6 samples from downstream Hackensack River exceeded 1 ppm Hg (maximum = 1.712 ppm); Hg in fish liver and kidney less in Berry's Creek than in Hackensack; Hg in crab muscle and shrimp less than 1.0 ppm in all samples; Hg in crab viscera exceeded 1.0 ppm in 2 samples from Berry's Creek (b) land animals: 15 mammals sampled near Berry's Creek; exceeded 1.0 ppm Hg in 4 fur samples (none of muscle tissues); invertebrates had less than 1 ppm Hg; 2 feather, 3 liver and 3 kidney samples from marsh birds and waterfowl exceeded 1 ppm Hg; none of muscle tissue samples exceeded 1 ppm; similar levels of Hg found in other areas of Meadowlands (c) vegetation: Hg in rhizome, stem, leaf, fruit generally higher than other areas; maximum = 7.9 ppm
1979-1980	Samples of killifish from 12 points in Berry's Creek showed less than 1.0 ppm Hg
Current (?)	New Jersey Marine Sciences Consortium (results not available)

[1] Standard for food consumption = 1 ppm Hg

How do the mercury values compare to N.J. & Federal standards.

so what?

AIR QUALITY

Studies were conducted in 1977 and 1978 by EPA for the N.J. Department of Environmental Protection (DEP) to measure mercury levels in the air at the site. The maximum daily average observed was 3.3 $\mu mg/m^3$ which is below the World Health Organization standard equivalent of 15 $\mu mg/m^3$/day. The conclusions drawn by the DEP (Lipsky, et al, undated) are that the levels are not high enough to be a health threat, but further monitoring is indicated.

HEALTH EFFECTS

One extensive epidemiological study by the Department of Health was conducted in the area of the Berry's Creek site. The investigation concluded that no apparent adverse health effects have resulted from the mercury present at the site or in the sediment, water and air near the site (Patel, 1980).

STABILITY OF SITE CONDITIONS

The monitoring programs reviewed for this study represent approximately ten years of record and indicate that the Berry's Creek area is stable and that the mercury continues to be preferentially bound to the soils and sediment of Berry's Creek. In the 50 year period since the start of mercury processing operations, there is no evidence for significant releases to the air, appreciable solubility in surface or groundwater, or adverse health effects. In addition, there appears to be no significant bioaccumulation of mercury from slow releases during the last 50 years. ?

The current stability of site conditions may be disturbed by changing the hydrology or geochemistry of the Creek. Hydrologic changes would consist of storm events which could act to resuspend the sediment, but which would also provide greater

maybe it's the storm events that are supplying the estuary with Hg.

How much?

dilution than would occur during dredging. Geochemical changes may include alterations in pH, salinity or oxidation-reduction conditions. Significant changes in the pH of the sediments and soils would be unlikely to occur, due to large buffering capacity of estuary sediments. In addition, neither pH nor salinity changes within the ranges expected for an estuary are expected to significantly alter the solubility of mercury. Mercury mobility is most likely to increase if the sediments are oxidized (Yeaple, et al, 1972). Since burial by filling seems more probable than drainage and aeration of the swamps and Creek, the most likely route of oxidation would be by turbulent mixing of the sediment and water in the presence of air, as would occur during dredging.

?

does CaCO3 is very low salinity

Why do estuarine sediments have a large buffering capacity?

MODELING OF THE GEOCHEMISTRY OF MERCURY

The chemical form of mercury in the environment strongly affects its mobility and toxicity. A critical question at this site is whether mercury concentrations in the water or food chain will increase as a result of dredging. Monitoring programs to date indicate that the mercury is not presently in a form which is easily adsorbed by plants or animals. Of the large quantities of mercury in the soils and sediments, only small amounts (slightly above background) have been observed dissolved in groundwater and surface water or present in the Berry's Creek biota. No evidence exists from the epidemiological survey for mercury toxicity or health effects to nearby residents.

Mercury (Hg) solubility may be increased by the conversion of relatively immobile or adsorbed forms to more soluble complexes. It is expected that liquid elemental mercury would have very low solubility (Lindsay, 1979), as would charged species of mercury which are strongly adsorbed by organic matter. The most soluble forms of mercury would be those with only weak residual charges (designated here as "zero charge complexes" for con-

venience). These complexes are only weakly attracted to oppositely charged particles of clay or organic matter in the soils and may be easily displaced by other, more strongly charged species. Hence, a strongly charged particle such as Na^+(sodium) or $HgCl^+$ (mercuric chloride) would displace $HgCl_2^o$.

Mercury toxicity may be increased by converting inorganic forms of mercury to methyl-mercury complexes. The rate of conversion under current conditions appears to be very low based on the only study of methyl-mercury concentrations (See Table 2). The low conversion rate may be due to the supression of bacterial growth by the very high levels of mercury or other metals present (Landa, 1978). The scant information available seems to support this conclusion. The ratio of methyl to total mercury is less for the high mercury concentrations (1/3590) than for the low mercury levels (1/692). The ratio in the highly contaminated sediment is also lower than the average ratio of 1/1000 in sediments, as estimated by Yeaple, et al (1972). More data points would be needed to confirm this conclusion. If mercury toxicity to bacteria does occur, then any reduction of mercury in the channel sediment (via dredging, natural dispersal of mercury laden particles, or increased mercury solubility) would increase the rate of methylation, the conversion of inorganic mercury to the more toxic methyl-mercury form.

The geochemistry of mercury in Berry's Creek was modeled during this study using the computer model GEOCHEM (Sposito and Mattigod, 1980). An average total mercury concentration of 1100 ppm was used. Results and assumptions used in the model are presented in Table 4, and in Tables A.1 and A.2 in the Appendix. The model predicted the presence of liquid elemental mercury and low mercury solubilities under current conditions, which corresponds to results and observations of the monitoring programs.

TABLE 4 - CALCULATED DISTRIBUTIONS OF MERCURY (Hg) SPECIES[1]

CASE MODELED	ASSUMED CONDITIONS[2]	CALCULATED CONCENTRATIONS OF SPECIES (ppm)[3]				%Hg AS "ZERO" CHARGED SPECIES[4]
Berry's Creek Sediment (Current Conditions)	pH = 7.3 Eh = -300mV Fe = Fe^{2+} S = S^{2-} N = NH_4^+	A. Short-term equilibrium				0.8%
		Hg (liq)	1082			
		$Hg(HS)_2^o$	8.73			
		HgS_2^{2-}	7.78			
		$Hg(HS)_2S^{2-}$	0.68			
		$Hg(HS)_3^-$	0.34			
		$HgH(HS)_4^-$	0.076			
		CH_3HgS^-	0.015			
		B. Long-term Equilibrium				0.0%
		Hg(liq)	937			
		HgS(solid)	163			
		$(CH_3Hg)_2S^o$	0.007			
Sediment mixed with water in Berry's Creek (dilution not considered)	pH = 7.3 Eh = +500mV Fe = Fe^{3+} S = SO_4^{2-} N = NO_3^-	A. Short-term Equilibrium				95.3%
		$HgCl_2^o$	647	$HgBr_2^o$	1.95	
		$Hg(OH)_2^o$	399	$HgCl^+$	0.016	
		$HgCl_3^-$	42.8	$HgCH_3Cl^o$	0.015	
		$HgCl_4^{2-}$	2.24	$HgOH^+$	0.003	
				$HgBr^+$	0.002	
		B. Long term Equilibrium				83.7%
		$HgCl_2^o$	604	$HgBr^+$	1.91	
		$Hg(OH)_2^o$	317	$HgCH_3Cl^o$	0.015	
		$Hg(OH)_2$(Solid)	115	$HgCl^+$	0.014	
		$HgCl_3^-$	41.8	$HgOH^+$	0.003	
		$HgCl_4^-$	2.40	$HgBr_3^-$	0.002	

[1] Total Hg Assumed Equal to 1110 ppm, total methylated mercury assumed to be .015 ppm.

[2] See Appendix A

[3] Concentrations in terms of ppm Hg.
Only species whose calculated concentrations exceeded drinking water standards (.002 ppm) are listed. Concentrations of solids based on the equivalent concentration in solution.

[4] "zero" charged species actually have a weak, residual charge (See text)

For the dredging case, it was assumed that the sediment was thoroughly mixed with the slightly saline water in Berry's Creek. Oxidizing conditions were also assumed. It should be noted that chemically oxidizing conditions do not necessarily correspond to the general water quality parameters of BOD or dissolved oxygen, which are based on aquatic life requirements. Results indicate that substantial percentages of mercury could be present in the soluble and poorly adsorbed (i.e. "zero-charge") forms under dredging conditions. Increased solubility would be expected to increase the mobility and possibly the rate of conversion of inorganic mercury to methyl-mercury. Since the precise value of some of the chemical parameters were not known, a number of cases representing extreme conditions for these types of environments were also modeled. The results of these parametric studies do not substantially alter the conclusions here stated.

In general, the trends predicted by the model agree with a laboratory study of the effects of dredging on mercury solubility (Yeaple, et al, 1972). Mercury solubility after a simulated dredging operation in a fresh water organic peat increased by a factor of approximately 14. Increased salinity would be expected to further increase mercury solubility, based on the geochemical model. The effect of dilution of mercury by stream water was included in the laboratory study but was not considered in the geochemical model since flow data from Berry's Creek is not currently available. Hence, the concentrations indicated for the model of the oxidized case should be used with caution. A concentration of 1000 ppm of mercury in solution would have to be diluted in a ratio of 1 part of 500,000 to meet drinking water standards, which appears unlikely under normal Berry's Creek flow conditions.

CONCLUSIONS

Results of the monitoring programs by other investigations indicate that contamination of site soils, channel sediments

and marsh soils has occurred in the vicinity of Berry's Creek. Interpretation of the soil and sediment data is hindered by the lack of support data and descriptions of the materials sampled. Biological, health and air quality analyses generally indicate mercury concentrations above normal levels, but not within the range of imminent health or environmental hazard.

Modeling of the geochemistry of mercury suggests that solubility and mobility of mercury may increase substantially when the sediment is mixed with Berry's Creek water during dredging. Reduction in the mercury level in the creek sediment due to dredging may also result in increased microbiological conversion of mercury to the more toxic methyl-mercury form.

It is our conclusion, based on available data and the geochemical modeling, that dredging may result in adverse impacts to the Berry's Creek area. Current conditions appear to be stable with no significant environmental impacts, and we recommend that the remedial program should be designed to maintain or enhance current stability, rather than reduce it. Site conditions should be further evaluated to confirm assumptions used in the geochemical model and to evaluate the feasibility and effectiveness of alternative actions prior to implementation of any remedial design.

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APPENDIX

A

APPENDIX A - MODEL STUDY ASSUMPTIONS AND ADDITIONAL CASES

The geochemistry of mercury distribution in Berry's Creek was modeled using a number of assumptions. Where possible, these assumptions were based on available data from previous studies at Berry's Creek or field conditions observed during the site visit. Other conditions were inferred to exist based on published studies of similar environments. Table A.1 outlines in greater detail the basis for the various assumptions.

In those cases where uncertainty exists, a range of parameter values beyond the expected conditions was investigated. This type of parmetric study provides insight into the variation in results which may occur if the site conditions are somewhat different from those expected. Table A.2 presents the results from cases in which the extent of oxidation (Eh), the acidity (pH), and the salinity was varied over anticipated extremes in the natural environment.

How much does Salinity vary over project area? If very little, these assumptions are ok. It would be preferable to break dredging area into compart

TABLE A.1 - ASSUMPTIONS USED IN MODELING THE GEOCHEMISTRY OF MERCURY

PARAMETER	BASIS OF ASSUMPTION
Total Salinity	The lowest salinity in upper Berry's Creek was measured by HMDC to be 0.1 parts per thousand. That value is assumed for Berry's Creek. Two other values, equal to sea water and 1/10,000 of sea water, are used as upper and lower limits
Distribution of primary salts	Same as sea water (Hem, 1970)
pH	Assumed to be equal to 7.3 in the Berry's Creek sediment, based on (a) published pH values for estuary soils (DeLaune, et al, 1981) and saline peat bogs (Becking, et al, 1960), and (b) the presence of H_2S (observed in the field in the lower portion of the organic-rich horizon). Upper and lower bounds on pH (9.0 and 6.0, respectively) are based on published ranges of marginal marine sediments (Becking, et al, 1960).
Eh	Assumed to be between 0 mV and -300 mV in the organic rich sediments, based on observation of H_2S and iron hydroxide in the field. An Eh of -300 mV also corresponds to the lowest reading expected in a marine near-shore sediment (Becking et al, 1960). An Eh value of +500 mV is assumed for the water in Berry's Creek, based on published ranges for surface streams. The less severely reduced environment (Eh = 0 mV) is also modeled.
CO_2	Assumed to be essentially zero (10^{-8} atm) in the sediment and in equilibrium with air ($10^{-3.5}$ atm) in the water in Berry's Creek
N,Fe,Mn	Set equal to the concentrations observed in another estuary soil (DeLaune, et al, 1981).

PARAMETER	BASIS OF ASSUMPTION
Hg, CH_3Hg^+	The total mercury and methyl-mercury contents are set equal to 1100 ppm (an average of the soil mercury levels) and 15 ppb (approximate highest observed methyl-mercury level in the previous monitoring programs).
Valence State of Fe, S, N	Based on Eh and pH of case modeled.

TABLE A.2 - CALCULATION MERCURY DISTRIBUTIONS FOR ADDITIONAL CASES MODELED

Case Modeled	Assumed Conditions[1]	Calculated Concentrations (ppm)[2]	%Hg As "Zero" Charged Species[3]
Sediment mixed with oxidized Creek water, Alkaline Conditions (dilution not considered)	pH = 9.0 Eh = +500mV Fe = Fe^{3+} S = SO_4^{2-} N = NO_3^-	A. Short-term Equilibrium $Hg(OH)_2^o$ 1097 $HgBr_2^o$ 0.066 $HgCl_2^o$ 2.40 $HgCl_4^{2-}$ 0.030 $HgCl_3^-$ .296 $HgCH_4Cl^o$ 0.015	99.9%
		B. Long-term Equilibrium $Hg(OH)_2$(solid) 778 $Hg(OH)_2^o$ 317 $HgBr_2^o$ 0.020 $HgCl_2^o$ 0.71 $HgCH_3Cl^o$ 0.015 $HgCl_3^-$ .085 $HgCl_4^{2-}$ 0.009	28.9%
Increased Salinity, Oxidized Conditions (i.e. sea-water and sediment mix, dilution not considered)	pH = 7.3 Eh = +500 mV Fe = Fe^{3+} S = SO_4^{2-} N = NO_3^- Total Salinity = Seawater	A. Short- or Long-term Equilibrium $HgCl_4^{2-}$ 834 HgI^+ 0.041 $HgCl_3^-$ 214 $Hg(OH)_2^o$ 0.019 $HgCl_2^o$ 53.8 $HgCH_3Cl^o$ 0.014 $HgBr_2^o$ 2.19 $HgBr_4^{2-}$ 0.009 $HgBr_3^-$ 0.502	5.1%
Decreased Salinity, Oxidized Conditions (i.e. fresh water and sediment mix, dilution not considered	pH = 7.3 Eh = +500mV Fe = Fe^{3+} S = SO^{2-} N = NH_4^+ Total Salinity = 1/10,000 X Seawater	A. Short- or Long-term Equilibrium $Hg(OH)_2^o$ 873 $Hg(OH)^+$ 0.007 Hg(liq) 194 $Hg(NH_3)_3^{2+}$ 0.005 $Hg(NH_3)_2^{2+}$ 31.7 $HgNH_3^{2+}$ 0.003 $HgCl_2^o$ 0.081 $HgCH_3NH_3^{2+}$ 0.014	79.4%

1 See Appendix

2 Concentrations in terms of ppm Hg.
Only species whose calculated concentrations exceeded drinking water standards (0.002 ppm) are listed. Concentrations of solids based on the equivalent concentration in solution. Total Hg assumed equal to 1110 ppm. Total methylated mercury assumed to be .015 ppm.

3 "Zero" charged species actually have a weak, residual charge (See text).

define oxidized. 100% saturation? AVERAGE [DO]?

NOT REALISTIC!

mo[re] realis[tic] ru[n] ∴ close to real pH & sal[inity]

How much water is assumed to be mixed with the sediment? Was model run with realistic dilution factors?

823390030

TABLE A.2 - CALCULATION MERCURY DISTRIBUTIONS FOR ADDITIONAL CASES MODELED

Case Modeled	Assumed Conditions[1]	Calculated Concentrations (ppm)[2]	%Hg As "Zero" Charged Species[3]
Sediment Severely Reduced, Acidic Conditions	pH = 6.0 Eh = -300mV Fe = Fe^{2+} S = S^{2-} N = NH_4^+	A. Short-term Equilibrium $Hg(liq)$ 1099 — $HgCH_3S^-$ 0.010 $Hg(HS)_2^o$ 0.39 — $Hg(HS)_3^-$ 0.003 $HgH(HS)_3^{2-}$ 0.015 — $(HgCH_3)_2S^o$ 0.002	0.04%
		B. Long-term Equilibrium $Hg(liq)$ 937 $HgS(solid)$ 162 $(HgCH_3)_2S^o$ .007	0.0%
Sediment Severely Reduced, Alkaline Conditions	pH = 9.0 Eh = -300mV Fe = Fe^{3+} S = $S_2O_3^{2-}$ N = NH_4^+	A. Short- or Long-term Equilibrium Hg (liq) 1100 ppm $HgCH_3S_2O_3^-$ 0.015 ppm	0.0%
Sediment Mildly Reduced, Near Neutral pH	pH = 7.3 Eh = 0mV Fe = Fe^{3+} S = $S_2O_3^{2-}$ N = NH_4^+	A. Short- or Long-term Equilibrium $Hg(liq)$ 960 $HgS_2O_3^o$ 132 $Hg(S_2O_3)_2^{2-}$ 7.6 $HgCH_3S_2O_3^-$ 0.015	12.0%
Sediment mixed with oxidized Creek water, Acidic conditions (dilution not considered)	pH = 6.0 Eh = +500mV Fe = Fe^{3+} S = SO_4^{2-} N = NH_4^+	A. Short- or Long-term Equilibrium $HgCl_2^o$ 873 — $HgCl_4^{2-}$ 1.63 $Hg(liq)$ 173 — $HgCl^+$ 0.030 $HgCl_3^-$ 41.8 — $HgCH_3Cl^o$ 0.015 $Hg(OH)_2^o$ 2.35 — $HgBr^+$ 0.003 $HgBr_2^o$ 2.09	79.8%

APPENDIX

B

FIGURES

TABLES

ABSTRACT

The description and use of GEOCHEM, a computer program for predicting the distribution of chemical species in soil systems, are discussed in considerable detail, including typical chemical equilibrium computations for actual soil solutions. The equilibria that can be calculated by the program are complexation, precipitation, oxidation-reduction, cation exchange, and metal ion adsorption. Thermodynamic data at 25° C and 1 atm pressure are stored in the data file of the program for combinations between 36 metals and 69 ligands that are of interest in soil solutions. Corrections for ionic strength up to 3 M can be made. Illustrative applications are presented for a number of important chemical phenomena associated with wastewater disposal on land.

CONTENTS

SECTION 1

INTRODUCTION

DEVELOPMENT OF THE PROGRAM

GEOCHEM is a multipurpose computer program for calculating the equilibrium speciation of the chemical elements in a soil solution. The method of calculation employed in the program is based on chemical thermodynamics. For each component of a soil solution, a mole balance equation is set up, and thermodynamic equilibrium constants corrected for ionic strength are incorporated into the various terms of this equation according to the law of mass action. The solution of the set of non-linear algebraic equations that results from mole balance applied to all the components simultaneously ultimately provides the concentration of each dissolved, solid, and adsorbed species in the soil system under consideration. Some typical applications of GEOCHEM would include: (1) prediction of the concentrations of inorganic and organic complexes of a metal cation in a soil solution, (2) calculation of the concentration of a particular chemical form of a nutrient element in a solution bathing plant roots so as to correlate that form with nutrient uptake, (3) prediction of the fate of a pollutant metal added to a soil solution of known characteristics, and (4) estimation of the effect of changing pH, ionic strength, redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil solution.

GEOCHEM is a modified version of the computer program REDEQL2, which was developed at the California Institute of Technology by F.M.M. Morel, R. E. McDuff, and J. J. Morgan. The detailed structure of REDEQL2 has been described in several published articles (Morel and Morgan, 1972; Morel et al., 1973; Morel and Yeasted, 1977) and in two reports (McDuff and Morel, 1973; Ingle et al., 1978). The methods of numerical analysis employed in the program are discussed by Morel and Morgan (1972) and are compared with the methods used in other computer programs by Leggett (1977). The potential user of GEOCHEM would be well advised to study these articles, and especially the two reports, for more than a casual understanding of the development of the program. GEOCHEM differs from REDEQL2 principally in the following ways: (1) It contains more than twice as many thermodynamic data, (2) it utilizes thermodynamic data that have been critically selected especially for soil systems, (3) it contains a method for describing cation exchange, and (4) it employs a different subroutine for correcting thermodynamic equilibrium constants for the effect of nonzero ionic strength.

GEOCHEM: A COMPUTER PROGRAM FOR THE CALCULATION OF CHEMICAL EQUILIBRIA IN SOIL SOLUTIONS AND OTHER NATURAL WATER SYSTEMS

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The Kearney Foundation of Soil Science

University of California

1980

GENERAL FEATURES OF THE PROGRAM

GEOCHEM is written in IBM 370 FORTRAN IV and requires about 200K of core. For any soil solution data to be analyzed by the program, the chemical components are identified as metals and unprotonated ligands. The principal variables considered by the program are the free ionic concentrations of the metals and ligands. Thus, e.g., the mole balance equation for a metal M, in the absence of precipitation-dissolution phenomena, is written in the form:

$$M_T = [M^{n+}] + \Sigma \alpha\, {}^{c}K_{\alpha\gamma\beta}\, [M^{n+}]^{\alpha}\, [H^{+}]^{\gamma}\, [L^{p-}]^{\beta} \qquad (1)$$

where M_T is the total molar concentration of the metal, [ ] refers to a molar concentration, ${}^{c}K_{\alpha\gamma\beta}$ is the conditional stability constant for the complex, $M_\alpha H_\gamma L_\beta$, H refers to the proton, and L refers to a ligand. The conditional stability constants ${}^{c}K_{\alpha\gamma\beta}$ are discussed in section 2, as is the notation employed for a complex. The point to be made here is that Eq. (1) and the analogous expression for the total molar concentration of a ligand, L_T, are nonlinear algebraic equations in the free ionic concentrations. The numerical analysis problem solved by GEOCHEM is to calculate the set of free ionic concentrations that satisfies a given set of mole balance equations (one equation for each metal and each ligand in the system being investigated), subject to input values of the M_T and L_T and the values of the thermodynamic equilibrium constants $K_{\alpha\gamma\beta}$ which are stored in the program. During the computation, the ionic strength is calculated using the current values of the concentrations of all charged species that are possible and the ${}^{c}K_{\alpha\gamma\beta}$ are computed in the usual way from the values of the $K_{\alpha\gamma\beta}$ with the help of single-ion activity coefficients (see, e.g., Stumm and Morgan, 1970). Thus the computer calculation is done self-consistently, with the total analytical concentrations and the thermodynamic equilibrium constants corrected for ionic strength related through mole balance.

GEOCHEM currently stores thermodynamic data for 36 metals and 69 ligands. These metals and ligands are listed as follows, along with their code numbers (also called "INMAT numbers") and code symbols.

Metals

1. Ca^{2+}	8. Mn^{2+}	15. Pb^{2+}	22. Li^{+}	29. Ce^{3+}
2. Mg^{2+}	9. Cu^{2+}	16. Co^{2+}	23. Be^{2+}	30. Au^{+}
3. Sr^{2+}	10. Ba^{2+}	17. Co^{3+}	24. Sc^{3+}	31. Th^{4+}
4. K^{+}	11. Cd^{2+}	18. Ag^{+}	25. TiO^{2+}	32. UO_2^{2+}
5. Na^{+}	12. Zn^{2+}	19. Cr^{3+}	26. Sn^{2+}	33. Cu^{+}
6. Fe^{3+}	13. Ni^{2+}	20. Al^{3+}	27. Sn^{4+}	34. CH_3Hg^{+}
7. Fe^{2+}	14. Hg^{2+}	21. Cs^{+}	28. La^{3+}	35. Rb^{+}
				50. H^{+}

Ligands*

1. CO_3^{2-}	13. $S_2O_3^{2-}$	25. $GLUT^{2-}$
2. SO_4^{2-}	14. CN^{-}	26. PIC^{-}
3. Cl^{-}	15. AC^{-}	27. NTA^{3-}
4. F^{-}	16. $ACAC^{-}$	28. $EDTA^{4-}$
5. Br^{-}	17. CIT^{3-}	29. $DCTA^{4-}$
6. I^{-}	18. OX^{2-}	30. $CYST^{2-}$
7. NH_3^{0}	19. SAL^{2-}	31. NOC^{3-}
8. S^{2-}	20. $TART^{2-}$	32. $PHTH^{2-}$
9. PO_4^{3-}	21. EN^{0}	33. ARG^{-}
10. $P_2O_7^{4-}$	22. DIP^{0}	34. ORN^{-}
11. $P_3O_{10}^{5-}$	23. $SUSAL^{3-}$	35. LYS^{-}
12. $SiO_2(OH)_2^{2-}$	24. GLY^{-}	36. HIS^{-}

37. ASP^-
38. SER^-
39. ALA^-
40. TYR^{2-}
41. MET^-
42. VAL^-
43. THR^-
44. PHE^-
45. ISO^-
46. LEU^-
47. PRO^-
48. $B(OH)_4^-$
49. SO_3^{2-}
50. SCN^-
51. NH_2OH
52. MoO_4^{2-}
53. WO_4^{2-}
54. AsO_4^{3-}
55. HVO_4^{2-}
56. SeO_3^{2-}
57. NO_3^-
58. $DTPA^{5-}$
59. SeO_4^{2-}
60. MAL^{2-}
61. BES^-
62. ClO_4^-
63. $CBER^-$
64. $CHAM^-$
65. FOR^-
66. $FUL1^-$
67. $FUL2^-$
68. $EDHG^{4-}$
90. ADS1
91. ADS2
92. ADS3
93. ADS4
94. ADS5
99. OH^-

---

* AC = acetate
ACAC = acetylacetate
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = ethylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLUT = glutamate
PIC = picolinate
NTA = nitrilotriacetate
EDTA = ethylenediaminetetraacetate
DCTA = 1,2-diaminocyclohexane-tetracetate
CYST = cysteine
NOC = nocardamine (desferri-ferrioxamine)
PHTH = phthalate
ARG = arginine
ORN = ornithine
LYS = lysine
HIS = histidine

DTPA = diethylenetriamine-pentaacetate
ASP = aspartate
SER = serine
ALA = alanine
TYR = tyrosine
MET = methionine
VAL = valine
THR = threonine
PHE = phenylalanine
ISO = isoleucine
LEU = leucine
PRO = proline
MAL = maleate
BES = benzylsulfonate
CBER = Camp Berteau montmorillonite
CHAM = Chambers bentonite
FOR = formate
FUL1 = fulvic acid ligand
FUL2 = fulvic acid ligand
EDHG = EDDHA = ethylene dihydroxyphenyl glycine
ADS1-ADS5 = adsorption surfaces

For a given metal-ligand combination, up to six soluble complexes and up to three solids can be considered by the program. In addition to the three solids per metal-ligand combination, mixed solids containing more than one metal or ligand are included in the program as indicated in Table 1. Formation constants for up to 20 mixed solids may be incorporated into GEOCHEM; at present there are 18 included.

GEOCHEM can describe soil solution equilibria in which the partial pressures of N_2, O_2, and CO_2 are permitted to vary (see section 6). The variation in O_2 pressure is treated as an oxidation-reduction phenomenon through the inclusion of 24 redox equations in the program. These redox equations are listed in Table 2. A full discussion of redox equilibria is given in section 4 of this report.

There are several specific characteristics of GEOCHEM that should be kept in mind as the description of how to use the program is read. These characteristics are most conveniently emphasized by the following list:

(1) The data bank of GEOCHEM consists of thermodynamic data at 25°C and 1 atmosphere. Therefore, all equilibrium calculations are performed at this fixed temperature and pressure. It is possible for a user to run equilibrium computations on GEOCHEM at temperatures and pressures other than 25°C and 1 atmosphere provided that a separate data bank is compiled by the user for the temperature and pressure of interest.

(2) An accounting for metastable species and species that are not favored kinetically can be incorporated into the computation by methods which are described in sections 2 through 6. It is not necessary to assume complete thermodynamic equilibrium in order to do a calculation.

(3) The condition of electroneutrality is <u>not</u> imposed during a computation performed by GEOCHEM. The only constraint imposed is that of mole balance (i.e., mass conservation), as discussed above. The fact that charge conservation is not considered by the program has the advantage that analytical data in which, for reasons of experimental error or omission, the equivalents of metals do not equal the equivalents of ligands may still be analyzed for speciation. On the other hand, there is no guarantee that the weighted sum of positively-charged species will equal the weighted sum of negatively-charged species according to the electroneutrality principle. This condition may be useful when examining the speciation results for a complete and accurate set of analytical data to see if the computer results are self-consistent. If electrical neutrality is violated, the thermodynamic data that were used may need revision or augmentation.

(4) Ionic strength corrections are made in the program through the use of single-ion or single-molecule activity coefficients. The equation employed to compute the activity coefficients (at 25°C) is:

TABLE 1. MIXED SOLIDS CONSIDERED BY GEOCHEM

Code No.	Code Name*	Code No.	Code Name*
1	CHLORITE	10	FECACARB
2	ILLITE	11	FECOCARB
3	MICCLINE	12	FEMNCARB
4	NA-MONT	13	FECUCARB
5	PBPO4CL	14	MUSCOVIT
6	FAPATITE	15	K-MONT
7	CDZNCARB	16	CA-MONT
8	CD3ZNCARB	17	MG-MONT
9	FENICARB	18	VERM

* CHLORITE = $Mg_5Al_2Si_3O_{10}(OH)_8$

MICCLINE = microcline

NA-MONT = $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

PBPO4CL = $Pb_5(PO_4)_3Cl$

FAPATITE = fluorapatite

CDZNCARB = $CdZn(CO_3)_2$

CD3ZNCARB = $Cd_3Zn(CO_3)_4$

FENICARB = $Fe_9Ni(CO_3)_{10}$

FECACARB = $Fe_9Ca(CO_3)_{10}$

FECOCARB = $Fe_9Co(CO_3)_{10}$

FEMNCARB = $Fe_4Mn(CO_3)_5$

FECUCARB = $Fe_4Cu(CO_3)_5$

MUSCOVIT = muscovite

K-MONT = $K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

CA-MONT = $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

MG-MONT = $Mg_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

VERM = Mg-vermiculite

pe = Eh/5.7152

TABLE 2. REDOX REACTIONS AND REDOX PARAMETERS IN GEOCHEM

Reaction No.	Reaction Type	M	L	CM	CL	NE*	NH†	Redox Reaction	log K	Reaction Name
1	-10	6	7	0	0	-1	0	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	13.0	FE2/FE3
2	-2	8	99	1	0	2	-4	$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e^-$	41.4	MNO2
3	-2	14	99	1	0	-2	0	$Hg^{2+} + 2e^- \rightarrow Hg(liq)$	29.0	HG(LIQ)
4	3	14	99	2	0	-2	0	$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}(aq)$	31.1	HG2+2
5	-2	15	99	1	0	2	-4	$Pb^{2+} + 2H_2O \rightarrow PbO_2(s) + 4H^+ + 2e^-$	-49.2	PBO2
6	-10	16	17	0	0	1	0	$Co^{2+} \rightarrow Co^{3+} + e^-$	-30.9	CO2/CO3
7	3	50	1	0	1	-4	0	$CO_3^{2-} + 6H^+ + 4e^- \rightarrow CH_2O(aq) + 2H_2O$	13.3	CH2O
8	10	2	8	0	0	-8	8	$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O$	20.2	SO4/S-2
9	10	7	57	0	0	8	-9	$NH_3(aq) + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e^-$	-88.1	NH3/NO3
10	1	50	99	0	0	2	-2	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	-60.0	H2O2
11	-10	26	27	0	0	2	0	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	-5.1	SN2/SN4
12	-2	7	8	1	2	2	0	$Fe^{2+} + 2S^{2-} \rightarrow FeS_2(s) + 2e^-$	45.3	FES2

Continued.

TABLE 2. (Continued)

Reaction No.	Reaction Type	M	L	CM	CL	NE	NH	Redox Reaction	log K	Reaction Name
13	-2	6	99	3	0	-1	-8	$3Fe^{3+} + 4H_2O + e^- \rightarrow Fe_3O_4(s) + 8H^+$	18.3	FE304
14	-3	8	99	3	0	2	-8	$3Mn^{2+} + 4H_2O \rightarrow Mn_3O_4(s) + 8H^+ + 2e^-$	-61.7	MN304
15	-1	8	99	1	0	1	-3	$Mn^{2+} + 2H_2O \rightarrow MnO(OH)(s) + 3H^+ + e^-$	-22.9	MnOOH
16	4	19	99	2	0	6	-14	$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$	-125.0	CR207
17	5	19	99	1	0	3	-7	$Cr^{3+} + 4H_2O \rightarrow HCrO_4^{2-} + 7H^+ + 3e^-$	-68.5	HCR04
18	6	19	99	1	0	3	-8	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^-$	-74.9	CR04
19	-1	50	8	0	1	2	0	$S^{2-} \rightarrow S(s) + 2e^-$	16.1	1S(S)
20	3	50	8	0	4	6	0	$4S^{2-} \rightarrow S_4^{2-} + 6e^-$	156.7	4S4-2
21	4	50	8	0	5	8	0	$5S^{2-} \rightarrow S_5^{2-} + 8e^-$	276.0	5S5-2
22	-10	33	9	0	0	1	0	$Cu^+ \rightarrow Cu^{2+} + e^-$	-2.6	CU1/CU2
23	-1	33	99	1	0	-1	0	$Cu^+ + e^- \rightarrow Cu(s)$	8.8	CU(S)
24	-1	50	57	0	1	-10	12	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O$	210.6	N2(G)

* NE = number of electrons produced in the reaction.

† NH = number of protons consumed in the reaction.

$$\log \gamma = -\frac{AZ^2\sqrt{I}}{1+aB\sqrt{I}} + B^{\circ}I \qquad (2)$$

where A = 0.5116 liter$^{\frac{1}{2}}$/mol$^{\frac{1}{2}}$, B = 0.3292 x 10^8 liter$^{\frac{1}{2}}$/cm mol$^{\frac{1}{2}}$, Z is the valence of the chemical species, and I is the true ionic strength in mol/liter. The values of the parameters $\underline{a}$ and B° in turn depend on the value of I:

(a) If I $\leq$ 0.5 mol/liter, a = 1/B and $B^{\circ} = 0.3AZ^2$. Thus Eq. (1.2) reduces to the Davies equation.

(b) If I > 0.5 mol/liter, B° = 0.041 liter/mol and $\underline{a}$ = 4 x 10^{-8} cm, 5 x 10^{-8} cm, and 6 x 10^{-8} cm for monovalent, bivalent, and trivalent ions, respectively. In this case, Eq. (2) becomes the Helgeson (1969) equation as modified by Truesdell and Jones (1973).

(c) For neutral species, at all values of I, B° = 0.1 liter/mole (see, e.g., Helgeson, 1969). Since Z = 0 in this case, the first term in Eq. (2) does not contribute to the calculation of .

INPUT DATA REQUIRED BY THE PROGRAM

To some extent the data which must be input to GEOCHEM in order for the program to do a speciation analysis depend on the type of problem to be considered. The general requirements are as follows:

(1) Total molar concentrations of each metal and each ligand.

(2) The pH value or the total net proton concentration in mol/liter. If the pH value is available, it should be used (see section 2).

(3) If solids are to be considered, a choice must be made as to which solid phases will be permitted to precipitate during the computation.

(4) If the soil solution is to be regarded as open with respect to CO_2, the partial pressure of this gas must be imposed.

(5) If redox equilibria are important, a choice of which redox half-reactions to allow must be made and the partial pressure of N_2 must be specified if NO_3^- is one of the ligands considered.

(6) The nature of adsorbing surfaces (PZC and other properties) must be specified if "specific adsorption" of metals is to be considered (see section 5).

THE INPUT DATA DECK

Table 3 summarizes the information that must appear on the card deck that is input to GEOCHEM. Each of the input data deck cards is discussed in detail in the section indicated parenthetically following the card format. This table should be consulted, after sections 2 through 7 have been read, as a convenient guide to preparing the input data.

TABLE 3. INFORMATION THAT MUST APPEAR ON A CARD DECK THAT IS INPUT TO GEOCHEM

Card No.	Card Columns	Type of Information Entered
(0)	Format I3,5X,E14.3 (Appendix).	
	1-3	ITMAX: Enter the maximum number of iterations permitted.
	4-8	Blank
	9-22	Enter convergence criterion: EPS = $\frac{\lvert\text{Calc. Tot. Conc.} - \text{Input Tot. Conc.}\rvert}{\text{Input Tot. Conc.}}$
(1)	Format 16I3. All blanks are read as zeros (section 2).	
	1-3	Number of metals including H^+
	4-6	Number of ligands including OH^-
	7-9	Number of cases to be considered. ($\leq$ 10). A case consists of total concentrations for a group of metals and ligands and pH or TOTH for that set of concentrations. Different p_{CO_2}, pE, and p_{N_2}, may also be specified. One or more of the above parameters may be varied from case to case. The number of metals or ligands cannot be changed although the input concentrations may be vanishingly small.
	10-12	Solid phases to consider. -1 means no solids may precipitate even when the solution is supersaturated.

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Type of Information Entered
		0 means no solids are imposed (assumed to be in contact with the solution) but any solid may precipitate if the solution is saturated with respect to it.
		N, where $0 < N \leq 13$, is the sum of those solids imposed and those not allowed to precipitate.
	13-15	Number of surfaces adsorbing ligands (enter "zero").
	16-18	Number of surfaces adsorbing metals.
	19-21	pH, calculated or fixed?
		0 means pH is specified for each case.
		1 means the program will compute pH for each case.
		Note: If this field is 1, TOTH data card is required.
	22-24	Redox reactions.
		0 means no redox reactions considered.
		1 means the program will include redox reactions.
		Note: If this field is 1, an electron activity card and a redox reaction card are required and a pN_2 card is required if NO_3^- is present.
	25-27	Mixed solids.
		0 means no mixed solids considered.
		1 means some mixed solids considered.
		Note: If this field is 1, a mixed solids card is required.
	28-30	Ionic strength.
		0 means the user specifies the ionic strength for the computer run (same value for all cases).
		1 means the program will compute the ionic strength for each case.
	31-33	Selects interaction intensity and/or capacity output routine.
		0 means no output.
		1 means interaction capacities computed and printed.
	_	2 means interaction intensities computed and printed.
		3 means both are printed.

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Type of Information Entered
	34-36	0 means output routine for case progress is used. 1 means suppressed.
	37-39	0 means output routine for complex concentrations is used. 1 means suppressed.
	40-42	0 means output routine for speciation of the ions is used. 1 means suppressed.
	43-45	0 means output routine for primary distribution of species is used. 1 means suppressed.
	46-48	0 means output routine for verification of thermodynamic data is used after each case when ionic strength is calculated. 1 means suppressed after each case.
(2) Ionic strength card. Format E7.2 (section 2).		
	1-7	Fixed or guessed ionic strength in units of mol/liter.
(3) Metal cards. No. of cards = no. of metals on Card No. 1 minus one. No card required for H^+. Format I2,2X,11(1X,F5.2) (section 2).		
	1-2	Code number of metal.
	6-10	Guess of the free concentration of the metal for the first case. Use -log molar concentration. If 0 is entered, the program assumes a value of 8 (i.e., 10^{-8} M).

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Type of Information Entered
The following fields are for the total concentration of the metals for up to ten cases.		
	12-16	First case. Use -log total molar concentration. If the first case is 0, program assumes 1 M total concentration. If any subsequent value is 0, the value from the previous case is used.
	18-22	Second case. Description for this case and the remaining cases is the same as for the first case.
	24-28	Third case.
	30-34	Fourth case.
	36-40	Fifth case.
	42-46	Sixth case.
	48-52	Seventh case.
	54-58	Eighth case.
	60-64	Ninth case.
	66-70	Tenth case.
(4) Ligand cards. No. of cards = no. of ligands on Card No. 1 minus one. No card reqired for OH^-. Format 12,2X, 11(1X,F5.2) (section 2).		
	1-2	Code number of ligand.
		Description identical to card (3) except for ligand instead of metal concentrations.
(5) pH card. Format 4X,10(1X,F5.2) (section 2).		
	6-10	Case 1 If pH is imposed, give pH for each case.

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Case	Type of Information Entered
	12-16	2	If pH is calculated, give a guess of pH
	18-22	3	for each case. If first case is 0,
	24-28	4	program assumes a value of 8. If any
	30-34	5	subsequent case is 0, the value from the
	36-40	6	previous case is used.
	42-46	7	
	48-52	8	
	54-58	9	
	60-64	10	
(5A)	TOTH CARD. Used only if pH calculated. Format 10E7.2 (section 2).		
	1-7	1	TOTH = net concentration of protons. A
	8-14	2	value must be given for each case, as a
	15-21	3	molar concentration (not -log M). A zero
	22-28	4	or blank means zero value for that case.
	29-35	5	
	36-42	6	
	43-49	7	
	50-56	8	
	57-63	9	
	64-70	10	
(6)	Partial pressure of CO_2 card. Used only if ligand 1, CO_3^{2-}, is included. Format 10F5.2 (sections 2 and 6).		
	1-5	1	Partial pressure of CO_2, pCO_2, is given
	6-10	2	as -log (pressure in atmospheres). If 0
	11-15	3	for the first case, no partial pressure
	16-20	4	is allowed. If any subsequent value is

Continued.

TABLE 3. (Continued)

Card No.	Card Columns		Type of Information Entered
	21-25	5	0, value from the preceding case is used.
	26-30	6	(Normal partial pressure is $10^{-3,5}$ atm.)
	31-35	7	
	36-40	8	
	41-45	9	
	46-50	10	

(7) Electron activity card. Used only if redox reactions considered. Format 10F5.2 (section 4).

$pE = \frac{Eh}{59.155}$

Case	
1-5, etc.	1, etc.

-log (electron activity), pE, must be given for each case. 0 means 0. Typical values range from -4 (reducing) to +12 (oxidizing).

(8) Partial pressure of N_2 card. Used only if redox reactions considered and if NO_3^- is included. Format 10F5.2 (section 4).

Case	
1-5, etc.	1, etc.

-log (partial pressure of N_2), pN_2, where the pressure is in atmospheres and is given for each case. If 0 for the first case, no partial pressure is allowed. If any subsequent value is 0, value from previous case is used. (Normal partial pressure is $10^{-0.1}$ atm.)

(9) Solids card. Used only if solids are imposed and/or not allowed to precipitate. Format 39I2 (section 3).

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Type of Information Entered
	1-2	Code number of metal in solid A.
	3-4	Code number of ligand in solid A.
	5-6	"1", "2", or "3", depending on whether A is the first, second or third solid listed in the Thermodynamic Data File, if this solid is imposed. If the solid is not allowed to precipitate, enter "-1", "-2", or "-3", depending on its position in the Thermodynamic Data File.
	7-8	Same set of 3 parameters in six columns for up to 13 solids.
	9-10	Solid B.
	11-12	
	13-14	
	15-16	Solid C, etc.
	17-18, etc.	
(10)	Redox reaction card. Used only if redox reactions considered. Format 21I2 (section 4).	
	1-2	First redox reaction considered. Enter reaction code number from Table 1.3. Up to 20 reactions, two columns/reaction.
	3-4	Second redox reaction.
	5-6	
(11)	Mixed solids card. Used only if mixed solids considered. May be blank. Format 20I4 (section 3).	
	1-4	Mixed solid reference number from Table 1.2. If the number is positive the solid is imposed. If the number is negative the solid is not allowed to precipitate. A mixed solid whose number is not given is allowed to precipitate. Up to 20 solids, 4 columns/solid.

Continued.

TABLE 3. (Continued)

Card No.	Card Columns	Type of Information Entered
	5-8 9-12	Second mixed solid.
(12), (13), (14)		Cards relating to specific adsorption reactions for metal cations. (see section 5).

SECTION 2

CHEMICAL SPECIATION IN SIMPLE SYSTEMS

INORGANIC SYSTEMS

One of the simpler applications of GEOCHEM is the calculation of the distribution of metals among several possible inorganic species in an extracted soil solution. In this case, there are no solid phases involved and the computation of the equilibrium condition of the solution requires only a partitioning of each metal present into free ionic, hydrolyzed, and inorganic complex forms according to the equations of mole balance and the thermodynamic complex stability constants that are appropriate for the system.

Table 4 lists analytical data obtained by routine laboratory methods for saturation extracts of three soils, Redding (Abruptic Durixeralf), Altamont (Typic Chromoxerert), and Hanford (Typic Xerorthent). These data give the total molar concentrations of the major metal and inorganic ligand constituents of the saturation extracts. This information, along with the pH values, is quite sufficient for a speciation calculation using GEOCHEM.

TABLE 4. ANALYTICAL DATA FOR SATURATION EXTRACTS OF THREE SOILS

Soil Series	pH	Ca_T	Mg_T	K_T	Na_T	CO_{3T}^*	SO_{4T}	Cl_T
		mol/liter x 10^3						
Redding	5.6	0.70	1.50	0.40	2.80	1.00	2.25	2.10
Altamont	6.9	2.50	0.80	0.60	1.00	2.00	2.50	1.00
Hanford	7.7	3.35	0.85	1.00	8.70	0.80	6.25	4.80

* $CO_{3T} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3^o]$, where [ ] refers to a molar concentration.

To set up the computation, the following cards must be punched:

a. Card No. 0. Format I3,5X,E14.8

Card columns	Type of information
1-3	ITMAX: Maximum number of iterations permitted.
4-8	Blank
9-22	EPS: Convergence Criterion: |Calculated Total Concentration - Input Total Concentration| - Input total concentration

b. Card No. 1. Format 16I3

Card columns	Type of information
1-3	Number of metals, including H^+ as a metal.
4-6	Number of ligands, including OH^- as a ligand.
7-9	Number of sets of concentration data ($\leq$ 10).
10-12	Enter "-1", meaning "no solid phases permitted".
13-15	Enter "0", meaning "no adsorption of ligands".
16-18	Enter "0", meaning "no adsorption of metals".
19-21	Enter "0", meaning "pH value is fixed".
22-24	Enter "0", meaning "no redox reactions".
25-27	Enter "0", meaning "no mixed solids".
28-30	Enter "1", meaning "ionic strength to be computed".
31-33	Enter "0", meaning "no interaction intensities or capacities to be computed".
34-36	Enter "0", meaning employ OUT 1".
37-39	Enter "0", meaning employ OUT 17".
40-42	Enter "0", meaning employ OUTMAT".
43-45	Enter "0", meaning employ OUT138".
46-48	Enter "0", meaning employ OUTCST".

Comments: Columns 28-30 instruct the program either to compute ("1") or not compute ("0") the ionic strength of the solution. OUT 1 is a subroutine that summarizes in a table the total and free ionic concentrations of the system components. OUT 17 tabulates the concentrations of the metal complexes as pC (= -log molar concentration) values. OUTMAT prints a matrix of the negative common logarithm of the sum of the concentrations of the complexes between each metal and all the ligands. OUT138 prints the mole percentage distribution of each system component among all the possible chemical forms it can have. OUTCST tabulates the thermodynamic data employed in the computation (as values of 10^2 log K) after they have been adjusted according to the value of the calculated ionic strength. Any of these output subroutines can be suppressed by entering "1" instead of "0" at the appropriate place in columns 34-48.

c. Card No. 2. Format E7.2

Enter a guess for the ionic strength, in mol/liter, for the first set of concentration data. If "0" were entered in columns 28-30 of Card No. 1, the ionic strength value entered on Card No. 2 would be that imposed as a fixed value for each equilibrium computation to be done.

d. Card No. 3A. Format I2,2X,11(1X,F5.2)

Card columns	Type of information
1-2	Enter the code number for one of the metal components as given in Section 1.
6-10	Enter a guess for the negative common logarithm of the molar free ionic concentration of the metal.
12-16	Enter the negative common logarithm of the total molar concentration of the metal (pC) for the first case.
18-22, etc.	Enter pC for the second case and continue similarly for the rest of the cases, up to 10.

e. Card No. 3B, etc.

Repeat what was entered on Card No. 3A for each metal being considered, except H^+. Do not prepare a card for H^+.

f. Card No. 4A, 4B, etc. Format I2,2X,11(1X,F5.2)

Repeat for each ligand component the kind of data that were entered on Cards 3A, 3B, etc. Do not include OH^- as one of the ligands.

g. Card No. 5. Format 4X,11(1X,F5.2)

Enter the pH values imposed for each of the sets of concentration data.

h. Card No. 6. Format 10F5.2

If CO_3 is one of the ligands in the system, the value "0" must be entered for each set of concentration data. This number is read by the program to mean "no partial pressure of CO_2 is imposed", i.e., the system is closed with respect to CO_2.

An example of the punched-card format for the saturation extract data is shown in Figure 1. In Tables 5-11 the output from GEOCHEM for the Redding soil extract is given. Note that 32 soluble complexes, including hydrolytic species, were possible in the soil solution, according to the thermodynamic data stored in the program. These complexes, according to Table 8, were carbonate, sulfate, chloride, and hydroxy complexes of the metal cations, including H^+. (The row of three digits following the value of pC for each complex in Table 8 is a "stoichiometric index" that indicates the number of metal atoms, the number of ligand atoms, and the number of H^+ or OH^-, respectively, in the complex. The third digit is positive if H^+ is present and is negative is OH^- is present in the complex.)

Now let us consider Tables 5-11 in more detail. Tables 5 and 11 list the output from the subroutine OUTCST. Table 5 a lists the equilibrium constants (as $10^2 \log {}^cK$, see description which follows) for various complexes, corrected for the guessed ionic strength listed on Card No. 2 (5.00E-3, see Table 4). These are the conditional constants with which the computations are initiated. In addition, ITMAX (maximum number of iterations permitted) and EPS (convergence criterion), listed on Card 1A (500 and 1.0E-4, respectively (see Figure 1)), are printed for verification. Table 11 lists the equilibrium constants (as $10^2 \log {}^cK$) corrected to the actual ionic strength of the solution (1.0438073E-02, Table 7), i.e., when the computations converged (ended).

The following description applies to both Table 5 and 11. The first two columns give the metal and ligand code numbers as taken from the list in Section 1. The columns listed under COMPLEXES give the values of $10^2 \log {}^cK$ followed by the three-digit stoichiometry indices for the complexes, where ${}^cK$ is the thermodynamic stability constant corrected to the ionic strength of the solution as calculated by the program. The stability constants ${}^cK$ describe chemical reactions of the form:

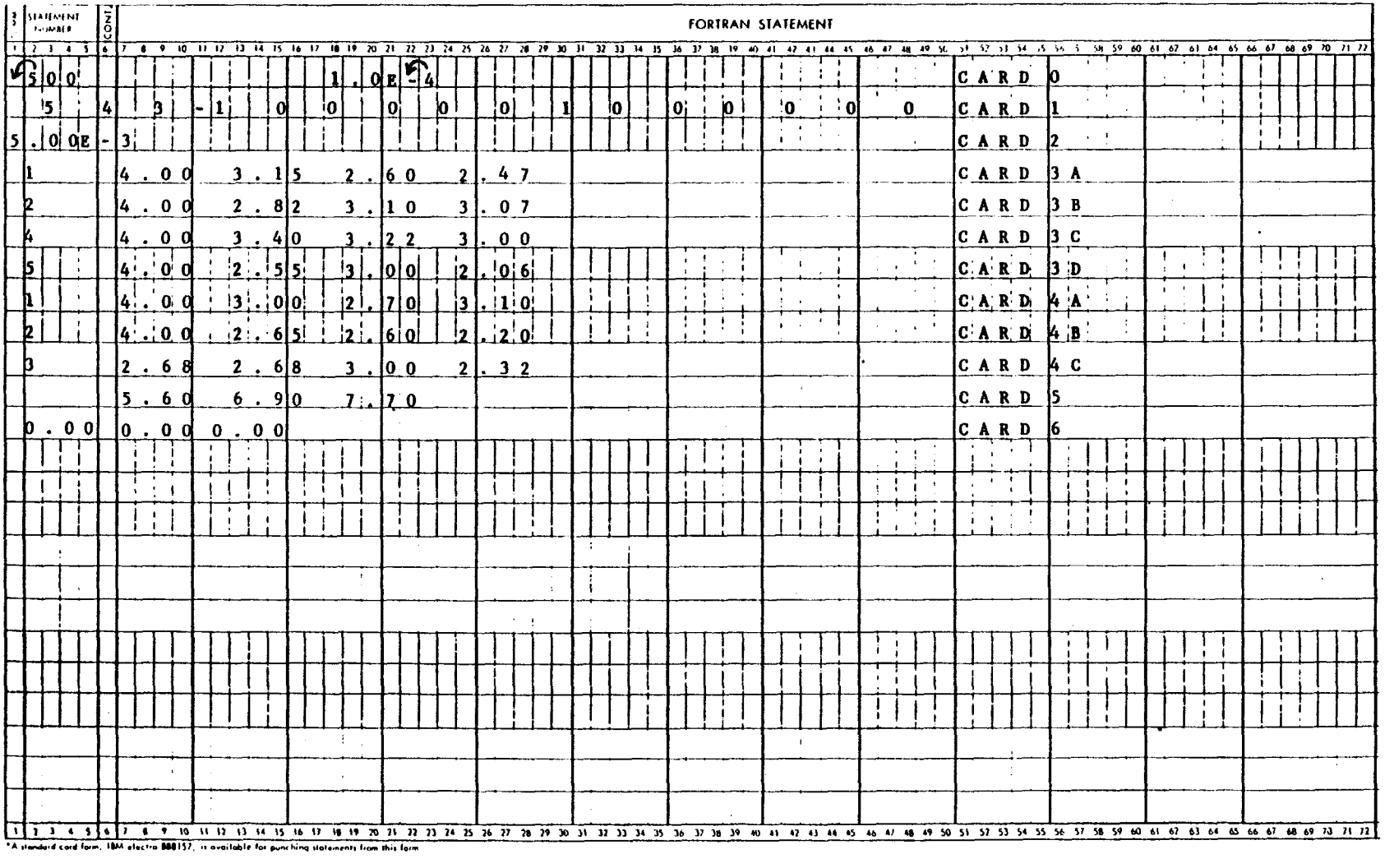
$$\alpha M + \beta L + \gamma H = M_\alpha H_\gamma L_\beta (aq) \qquad (3)$$

or

$$\alpha M + \beta L - \gamma OH + \gamma H_2O = M_\alpha OH_{-\gamma} L_\beta (aq) \qquad (4)$$

with the equilibrium constants

$$K = (M_\alpha H_\gamma L_\beta)/(M)^\alpha (H)^\gamma (L)^\beta \qquad (5)$$



*A standard card form, IBM electro 888157, is available for punching statements from this form

Figure 1. Punched-card format for the analytical data in Table 4.

TABLE 5. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEMS DESCRIBED IN TABLE 4.
(EQUILIBRIUM CONSTANTS CORRECTED ACCORDING TO THE GUESSED IONIC STRENGTH)

INPUT DATA FOR VERIFICATION

MET	LIG*	SOLID					*	COMPLEXES											*
1	1	0	0 0 0	0	0 0 0	0	0 0 0	293	1 1 0	1115	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	2	0	0 0 0	0	0 0 0	0	0 0 0	203	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	3	0	0 0 0	0	0 0 0	0	0 0 0	46	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	99	0	0 0 0	0	0 0 0	0	0 0 0	-1268	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	1	0	0 0 0	0	0 0 0	0	0 0 0	263	1 1 0	1105	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	2	0	0 0 0	0	0 0 0	0	0 0 0	193	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	3	0	0 0 0	0	0 0 0	0	0 0 0	36	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	99	0	0 0 0	0	0 0 0	0	0 0 0	-1188	1 0-1	-3963	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	1	0	0 0 0	0	0 0 0	0	0 0 0	76	1 1 0	1001	1 1 1	50	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	2	0	0 0 0	0	0 0 0	0	0 0 0	76	1 1 0	171	1 1 1	130	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	3	0	0 0 0	0	0 0 0	0	0 0 0	-36	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	99	0	0 0 0	0	0 0 0	0	0 0 0	-1451	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	1	0	0 0 0	0	0 0 0	0	0 0 0	46	1 1 0	1031	1 1 1	-89	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	2	0	0 0 0	0	0 0 0	0	0 0 0	96	1 1 0	181	1 1 1	130	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	3	0	0 0 0	0	0 0 0	0	0 0 0	-16	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	99	0	0 0 0	0	0 0 0	0	0 0 0	-1421	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	1	0	0 0 0	0	0 0 0	0	0 0 0	1018	0 1 1	1653	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	2	0	0 0 0	0	0 0 0	0	0 0 0	188	0 1 1	-846	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	3	0	0 0 0	0	0 0 0	0	0 0 0	-844	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	99	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0-0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0

ITMAX = 500 EPS = 0.99999990E-04

Since no solid phases were permitted to form in the computation, no data for the 7 possible solids were printed.

TABLE 6. DESCRIPTION OF THE SYSTEM AND INPUT DATA FOR THE SATURATION EXTRACTS

THESE COMPUTATIONS INVOLVE 5 METALS, 4 LIGANDS, 32 COMPLEXES AND 7 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

3 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT*	GUESS	TOTCC 1	TOTCC 2	TOTCC 3
CA	1	4.000	3.150	2.600	2.470
MG	2	4.000	2.820	3.100	3.070
K	3	4.000	3.400	3.220	3.000
NA	4	4.000	2.550	3.000	2.060

LIGAND	#INMAT*	GUESS	TOTCC 1	TOTCC 2	TOTCC 3
CO3-	1	4.000	3.000	2.700	3.100
SO4	2	4.000	2.650	2.600	2.200
CL	3	2.680	2.680	3.000	2.320
FIXED PH			5.600	6.900	7.700

* Code number for the metal or ligand from list in Section 1.

TABLE 7. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE REDDING SOIL

CASE NUMBER 1

NUMBER OF ITERATIONS = 6

NUMBER OF ITERATIONS = 9

NUMBER OF ITERATIONS = 11*

IONIC STRENGTH = 1.0438073E-02†

FIXED PH = 5.600 COMPUTED TOTH = 0.1843486E-02

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	6.0683535E-04	3.21693	7.0794765E-04	3.15000	5.5460370E-10
MG	1.3366558E-03	2.87398	1.5135657E-03	2.82000	8.8932528E-10
K	3.9391732E-04	3.40459	3.9810827E-04	3.40000	-1.9283981E-10
NA	2.7711806E-03	2.55733	2.8183921E-03	2.55000	-1.0688432E-10
CO3-	4.7274753E-09	8.32537	1.0000013E-03	3.00000	-5.5879354E-09
SO4	1.9248503E-03	2.71560	2.2387274E-03	2.65000	1.6734703E-09
CL	2.0764563E-03	2.68268	2.0893023E-03	2.68000	-1.4460963E-10

* The last "NUMBER OF ITERATIONS" is that required to obtain convergence. Previous values are those at the times the ionic strength was recalculated.

† In units of mol/liter.

TABLE 8. OUTPUT FROM THE SUBROUTINE OUT 17 FOR THE REDDING SOIL

Concentrations of Complexes*											
CA	CO3-	8.72	1	1	0	6.10	1	1	1		
CA	SO4	4.01	1	1	0						
CA	CL	5.50	1	1	0						
CA	OH	10.33	1	0	-1						
MG	CO3-	8.68	1	1	0	5.86	1	1	1		
MG	SO4	3.77	1	1	0						
MG	CL	5.26	1	1	0						
MG	OH	9.18	1	0	-1	28.69	4	0	-4		
K	CO3-	11.03	1	1	0	7.40	1	1	1	14.72	2 1 0
K	SO4	5.42	1	1	0	10.09	1	1	1	8.31	2 1 0
K	CL	6.47	1	1	0						
K	OH	12.31	1	0	-1						
NA	CO3-	10.48	1	1	0	6.25	1	1	1	14.40	2 1 0
NA	SO4	4.37	1	1	0	9.14	1	1	1	6.62	2 1 0
NA	CL	5.42	1	1	0						
NA	OH	11.17	1	0	-1						
H	CO3-	3.81	0	1	1	3.08	0	1	2		
H	SO4	6.50	0	1	1	22.44	0	1	2		
H	CL	16.73	0	1	1						

* Expressed as -log[ ], where [ ] refers to a molar concentration.

TABLE 9. OUTPUT FROM THE SUBROUTINE OUTMAT FOR THE REDDING SOIL

	FREE MET	CO3-	SO4	CL	OH
FREE LIG		8.33	2.72	2.68	8.35
CA	3.22	6.10	4.01	5.50	10.33
MG	2.87	5.86	3.77	5.26	9.18
K	3.40	7.40	5.42	6.47	12.31
NA	2.56	6.25	4.37	5.42	11.17
HYDROGEN	5.60*	3.00	6.50	16.73	*****

Free metal and free ligand concentrations are in negative logarithm of molarities.

Each entry in this table, except for those in the "FREE LIG" row and the "FREE MET" column, is a negative logarithm of the sum of the entries in a given row of Table 8, after their conversion to molar concentrations. For example, the entry for "HYDROGEN/CO3-" is 3.00 because $3.00 = -\log(10^{-3.81} + 10^{-3.08})$ according to the data in the "H CO3-" row of Table 8.

* pH value

TABLE 10. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE REDDING SOIL

PRIMARY DISTRIBUTION OF METALS AND LIGANDS *

CA	
AS A FREE METAL/	85.7 PERCENT
BOUND WITH CO3-/	0.1 PERCENT
BOUND WITH SO4 /	13.7 PERCENT
BOUND WITH CL /	0.4 PERCENT
MG	
AS A FREE METAL/	88.3 PERCENT
BOUND WITH SO4 /	11.2 PERCENT
BOUND WITH CL /	0.4 PERCENT
K	
AS A FREE METAL/	98.9 PERCENT
BOUND WITH SO4 /	1.0 PERCENT
NA	
AS A FREE METAL/	98.3 PERCENT
BOUND WITH SO4 /	1.5 PERCENT
BOUND WITH CL /	0.1 PERCENT
CO3-	
BOUND WITH MG /	0.1 PERCENT
BOUND WITH H /	99.7 PERCENT
SO4	
AS A FREE LIGAND/	86.0 PERCENT
BOUND WITH CA /	4.3 PERCENT
BOUND WITH MG /	7.6 PERCENT
BOUND WITH K /	0.2 PERCENT
BOUND WITH NA	1.9 PERCENT
CL	
AS A FREE LIGAND/	99.4 PERCENT
BOUND WITH CA /	0.2 PERCENT
BOUND WITH MG /	0.3 PERCENT
BOUND WITH NA /	0.2 PERCENT

* Only values greater than or equal to 0.1 mole percent are printed.

TABLE 11. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEMS DESCRIBED IN TABLE 4

(Constants Corrected to the Ionic Strength of the Solution when the Computations Converged)

INPUT DATA FOR VERIFICATION

MET	LIG *		SOLID				*					COMPLEXES					*
1	1	0	0 0 0	0	0 0 0	0	0 0 0	282	1 1 0	1104	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	2	0	0 0 0	0	0 0 0	0	0 0 0	192	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	3	0	0 0 0	0	0 0 0	0	0 0 0	40	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	99	0	0 0 0	0	0 0 0	0	0 0 0	-1271	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	1	0	0 0 0	0	0 0 0	0	0 0 0	252	1 1 0	1094	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	2	0	0 0 0	0	0 0 0	0	0 0 0	182	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	3	0	0 0 0	0	0 0 0	0	0 0 0	30	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	99	0	0 0 0	0	0 0 0	0	0 0 0	-1191	1 0-1	-3959	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	1	0	0 0 0	0	0 0 0	0	0 0 0	70	1 1 0	993	1 1 1	41	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	2	0	0 0 0	0	0 0 0	0	0 0 0	70	1 1 0	163	1 1 1	121	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	3	0	0 0 0	0	0 0 0	0	0 0 0	-38	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	99	0	0 0 0	0	0 0 0	0	0 0 0	-1451	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	1	0	0 0 0	0	0 0 0	0	0 0 0	40	1 1 0	1023	1 1 1	-96	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	2	0	0 0 0	0	0 0 0	0	0 0 0	90	1 1 0	173	1 1 1	121	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	3	0	0 0 0	0	0 0 0	0	0 0 0	-18	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	99	0	0 0 0	0	0 0 0	0	0 0 0	-1421	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	1	0	0 0 0	0	0 0 0	0	0 0 0	1012	0 1 1	1645	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	2	0	0 0 0	0	0 0 0	0	0 0 0	182	0 1 1	-852	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	3	0	0 0 0	0	0 0 0	0	0 0 0	-845	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	99	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0

Since no solid phases were permitted to form in the computation, no data for the seven possible solids were printed.

or

$$^{*}K = (M_{\alpha}OH_{-\gamma}L_{\beta})/(M)^{\alpha}(OH)^{-\gamma}(L)^{\beta} \qquad (6)$$

where M refers to the metal ion, L to the ligand, H to the proton, and OH to hydroxyl. The Greek letters are stoichiometric coefficients and ( ) refers to a thermodynamic activity. Equations 4 and 6 are employed only for hydrolytic species.

Table 6 indicates the number of chemical species, the initial guess for the ionic strength (in mol/liter), and the cases to be analyzed by the program. Table 7 applies only to the Redding soil extract (Case 1), indicating the output from the subroutine OUT 1. The true, calculated ionic strength is given along with the free ionic and total concentrations of each system component. The column headed "REMAINDER" list the values of the difference between the input total concentration of a component and the sum of the weighted concentrations of its free and complexed forms, divided by the input total concentration. This number must be less than 10^{-4} (EPS for these cases) in order for the computation to be convergent. Table 8 lists the output from the subroutine OUT 17. It may be seen that, for the Redding soil, complexes with SO_4^{2-} are the most significant ones for all the metals in the system. Table 9 gives the output from the subroutine OUTMAT, i.e., the negative logarithm of the sum of molar concentrations of, e.g., all carbonate complexes of Ca^{2+}, of Mg^{2+}, etc. Table 10 lists what is often the most useful output, the mole percentage distribution of each component among its possible chemical forms, based on the output from OUTMAT. GEOCHEM lists mole percentages only if they are at least 0.1% in value. In the case of the Redding soil, it is seen that the metals and ligands are primarily in the free ionic form, with the exception of CO_3^{2-} which is essentially all bicarbonate complex.

ORGANIC SYSTEMS

There is no difference of principle between the calculation of chemical equilibria for inorganic systems and systems that contain organic ligands. Equations 3 to 6 apply whether L refers to CO_3^{2-} or citrate, Cl^- or salicylate. Actually, the difference between soil solutions that contain organic compounds and those that do not is in the facts that the organic compounds in soil may be difficult to identify and characterize, that they may undergo transformations mediated biologically, and that they may form complexes of varying stoichiometry with the same metal.— Once the organic compound is identified and data are available concerning its metal complexes, it may be treated just the same as, e.g., CO_3^{2-} in a calculation performed by GEOCHEM.

Table 12 lists analytical data for a saturation extract of an Altamont soil to which sewage sludge and $CdSO_4$ had been added as part of a glasshouse experiment to study Cd uptake. In this example there were 9 metals (including H^+) and 15 ligands (including OH^-) that could form 261 different complexes, according to the thermodynamic data in the program. Nine of the ligands in Table 12 are organic compounds. The concentrations of these compounds were not determined analytically, but instead were selected to provide a mixture of organic acids whose overall pH titration curve closely resembled that found experimentally for the water soluble organic fraction of sewage sludge and whose total acidity was the same as that of the sludge organics when the concentration of the latter is 10^{-3} M. The organic acids selected are representative of the types of acidic, metal-complexing functional groups in water soluble sludge organics and the concentration of 10^{-3} M is typical of what is found for organic compounds in the Altamont soil solution after the incorporation of sewage sludge. In other words, the mixture of organic acids in Table 12 constitutes a model system for the soluble, metal-complexing organic compounds in the Altamont soil during the greenhouse experiment. A detailed description of the model organic system is provided in Mattigod and Sposito (1979).

The computer cards for this example are in every way similar to what was described earlier in this section, except that now there is only one case. This case, however, requires 8 metal cards and 14 ligand cards instead of 4 metal cards and 3 ligand cards as before. The same kinds of ionic strength, pH, and carbonate cards are required as for the inorganic system.

Table 13 shows the output from the subroutine OUT138 for this example. There is much interesting information in the percentage distribution figures for the metals and ligands, but what stands out is the strong complexation of Cu(II) and Fe(III) by the organic ligands, the relative lack of complexation of Cd,Mn(II), and Zn, and the absence of metal complexes with the amino acid components. The major cations, Ca, Na, and K, appear to be involved principally with the inorganic part of the system, while Cu(II) and Fe(III) are involved principally with the organic part, with the remaining minor cations, Cd, Mn(II), and Zn, falling somewhere in between.

SYSTEMS FOR WHICH THE pH VALUE IS UNKNOWN

There may be cases in which analytical data for a soil solution are available but the pH value of the solution is unknown. This situation could arise, e.g., if only the pH of a soil paste has been measured and cannot be extrapolated to get the pH of a saturation extract because of an unknown suspension effect, or if the analytical data have been obtained from a commercial laboratory where pH measurements are not routine. Another possibility is that the data to be analyzed with GEOCHEM

TABLE 12. ANALYTICAL DATA (EXPRESSED AS pC VALUES) FOR A SATURATION EXTRACT OF AN ALTAMONT SOIL AMENDED WITH SEWAGE SLUDGE AND $CdSO_4$

Component	pC*	Component	pC
Ca	2.07	CIT†	4.14
K	3.70	SAL	4.27
Na	3.00	PHTH	3.97
Fe(III)	4.75	ARG	4.49
Mn(II)	4.70	ORN	4.36
Cu(II)	5.72	LYS	4.36
Cd	5.85	VAL	4.36
Zn	5.13	NO	2.17
CO_3	2.70	MAL	3.97
SO_4	2.70	BES	4.27
Cl	2.28	pH = 6.30	4.27
PO_4	4.00		

* pC = -log[ ], where [ ] refers to a molar concentration.

† Code symbols for components are listed in Section 1.

TABLE 13. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE SLUDGE-AFFECTED ALTAMONT SOIL

Primary Distribution of Metals and Ligands

CA		
AS A FREE METAL	/	88.6 PERCENT
BOUND WITH CO3-	/	0.6 PERCENT
BOUND WITH SO4	/	6.9 PERCENT
BOUND WITH CL	/	1.0 PERCENT
BOUND WITH PO4	/	0.3 PERCENT
BOUND WITH CIT	/	0.7 PERCENT
BOUND WITH PHTH	/	0.6 PERCENT
BOUND WITH NO3	/	0.6 PERCENT
BOUND WITH MAL	/	0.6 PERCENT
K		
AS A FREE METAL	/	99.0 PERCENT
BOUND WITH SO4	/	0.6 PERCENT
BOUND WITH NO3	/	0.3 PERCENT
NA		
AS A FREE METAL	/	98.8 PERCENT
BOUND WITH CO3-	/	0.1 PERCENT
BOUND WITH SO4	/	0.9 PERCENT
BOUND WITH NO3	/	0.1 PERCENT
FE3		
BOUND WITH CO3-	/	20.6 PERCENT
BOUND WITH CIT	/	79.3 PERCENT
MN		
AS A FREE METAL	/	77.8 PERCENT
BOUND WITH CO3-	/	11.9 PERCENT
BOUND WITH SO4	/	6.1 PERCENT
BOUND WITH CL	/	0.2 PERCENT
BOUND WITH PO4	/	1.4 PERCENT
BOUND WITH CIT	/	0.4 PERCENT
BOUND WITH NO3	/	1.4 PERCENT
BOUND WITH MAL	/	0.9 PERCENT
BOUND WITH BES	/	0.1 PERCENT
CO3-		
BOUND WITH CA	/	2.6 PERCENT
BOUND WITH FE3	/	0.5 PERCENT
BOUND WITH MN	/	0.1 PERCENT
BOUND WITH H	/	96.6 PERCENT
SO4		
AS A FREE LIGAND	/	69.8 PERCENT
BOUND WITH CA	/	29.6 PERCENT
BOUND WITH NA	/	0.5 PERCENT
CL		
AS A FREE LIGAND	/	98.4 PERCENT
BOUND WITH CA	/	1.6 PERCENT
PO4		
BOUND WITH CA	/	22.3 PERCENT
BOUND WITH NA	/	0.1 PERCENT
BOUND WITH MN	/	0.3 PERCENT
BOUND WITH H	/	77.2 PERCENT
CIT		
BOUND WITH CA	/	76.9 PERCENT
BOUND WITH FE3	/	19.5 PERCENT
BOUND WITH CU2+	/	2.6 PERCENT
BOUND WITH H	/	0.9 PERCENT
SAL		
BOUND WITH CA	/	2.6 PERCENT
BOUND WITH H	/	97.4 PERCENT
PHTH		
AS A FREE LIGAND	/	46.4 PERCENT
BOUND WITH CA	/	49.4 PERCENT
BOUND WITH ZN	/	0.1 PERCENT
BOUND WITH H	/	4.0 PERCENT

Continued.

TABLE 13. (Continued)

CU2+		
AS A FREE METAL	/	0.3 PERCENT
BOUND WITH CO3-	/	0.1 PERCENT
BOUND WITH CIT	/	97.0 PERCENT
BOUND WITH ARG	/	1.1 PERCENT
BOUND WITH VAL	/	1.1 PERCENT
CD		
AS A FREE METAL	/	62.2 PERCENT
BOUND WITH CO3-	/	1.7 PERCENT
BOUND WITH SO4	/	4.9 PERCENT
BOUND WITH CL	/	17.2 PERCENT
BOUND WITH PO4	/	0.5 PERCENT
BOUND WITH CIT	/	4.5 PERCENT
BOUND WITH PHTH	/	4.4 PERCENT
BOUND WITH VAL	/	0.1 PERCENT
BOUND WITH NO3	/	1.1 PERCENT
BOUND WITH MAL	/	3.4 PERCENT
ZN		
AS A FREE METAL	/	69.9 PERCENT
BOUND WITH CO3-	/	18.5 PERCENT
BOUND WITH SO4	/	6.9 PERCENT
BOUND WITH CL	/	0.1 PERCENT
BOUND WITH PO4	/	0.7 PERCENT
BOUND WITH PHTH	/	2.0 PERCENT
BOUND WITH VAL	/	0.1 PERCENT
BOUND WITH MAL	/	1.6 PERCENT
BOUND WITH OH	/	0.1 PERCENT
ARG		
AS A FREE LIGAND	/	0.1 PERCENT
BOUND WITH H	/	99.8 PERCENT
ORN		
BOUND WITH H	/	100.0 PERCENT
LYS		
BOUND WITH H	/	100.0 PERCENT
VAL		
BOUND WITH H	/	99.9 PERCENT
NO3		
AS A FREE LIGAND	/	99.2 PERCENT
BOUND WITH CA	/	0.8 PERCENT
MAL		
AS A FREE LIGAND	/	27.5 PERCENT
BOUND WITH CA	/	49.8 PERCENT
BOUND WITH MN	/	0.2 PERCENT
BOUND WITH ZN	/	0.1 PERCENT
BOUND WITH H	/	22.4 PERCENT
BES		
AS A FREE LIGAND	/	87.4 PERCENT
BOUND WITH CA	/	12.6 PERCENT

may be composite data created for a special research purpose by adding together empirical concentration data for two solutions of very different composition (e.g., a saturation extract of a soil and an industrial wastewater). Even if the pH values of the two original solutions are available, the pH value of their mixture is not easily estimated with accuracy.

If the pH value must be computed by GEOCHEM, it is necessary to modify the computer card arrangement described earlier in this section in two ways. First, the number entered in columns 19-21 of Card No. 1 is changed to "1", meaning "pH value is to be computed", and the data entered on Card No. 5 now become gueses of the pH values for each of the sets of concentration data. These guesses play the same role as those for ionic strength in Card No. 2. The second modification is that a Card No. 5A must be inserted following Card No. 5. This new card may be described as follows:

Card No. 5A. Format 10E7.2

If pH is to be computed, enter a value for TOTH, in mol/liter, for each set of concentration data ($\leq$ 10).

The quantity TOTH is defined by the equation:

$$TOTH = \Sigma_n\,[acid] + [H^+] - \Sigma_m\,[base] - [OH^-] \qquad (7)$$

where [ ] refers to a molar concentration, "acid" refers to any species expected in the system that contains dissociable protons (n being the number of dissociable protons in the acid), and "base" refers to any species expected that contains dissociable hydroxyls (m being the number of dissociable hydroxyls in the base). In general, an acid is any compound with the formula H_nL, where L refers to a non-dissociable inorganic or organic ligand, as well as NH_4^+ CO_2, and SiO_2. A base is any compound with the formula $M(OH)_m$, where M refers to a metal, as well as any hydrolyzable metal oxide. Equation (7) is a statement of the "proton condition" for an aqueous solution whose components are unhydrolyzed metals and unprotonated ligands (see, e.g., Morel and Morgan, 1972; Stumm and Morgan, 1970, p. 88).

The method of calculation of TOTH can be made clear by considering some specific examples.

a. A solution containing Na_2CO_3, NaH_2PO_4, $Ca(OH)_2$, and $CaCO_3$.

$$TOTH = [NaHCO_3] + 2[NaH_2PO_4] - 2[Ca(OH)_2]$$

Note that the computation does not include Na_2CO_3 or $CaCO_3$ and that the molar concentration of $NaHCO_3$ has to be estimated in some way. This

could be accomplished by a good guess of the pH value and a subsequent estimate of the partitioning of CO_{3T} into $[CO_3^{2-}]$, $[HCO_3^-]$, and $[H_2CO_3]$. Even better would be a direct titrimetric determination of $[HCO_3^-]$ in the solution.

b. A solution containing dissolved CO_2 and Al_2O_3.

$$TOTH = 2[CO_2] - 6[Al_2O_3]$$

In this case the hydration of CO_2 to produce H_2CO_3 adds 2 protons per CO_2 molecule and the hydrolysis of Al_2O_3 to produce $2Al(OH)_3$ adds 6 hydroxyls per Al_2O_3 molecule.

c. A solution containing Al_2O_3, SiO_2, NH_4Cl, and CH_3CO_2H.

$$TOTH = 2[SiO_2] + [NH_4Cl] + [CH_3CO_2H] - 6[Al_2O_3]$$

Here the hydration of SiO_2 to produce H_4SiO_4 contributes 2 dissociable protons per SiO_2 molecule, $NH_4Cl = NH_3 \cdot HCl$ and acetic acid each contribute 1 dissociable proton per molecule, and the hydrolysis of Al_2O_3 contributes 6 OH^- as before.

It should be noted that TOTH need not be a positive number. In Example b, if the molar concentrations of CO_2 and Al_2O_3 happened to be the same, TOTH would equal $-4[Al_2O_3]$. For systems in which carbonate salts are present, it is best to have an experimental determination of the bicarbonate concentration if TOTH must be computed. Further discussion of TOTH is given by Ingle *et al.* (1978) and Morel and Morgan (1972).

SECTION 3

SOLUBILITY EQUILIBRIA

CALCULATIONS WITHOUT IMPOSED SOLIDS

Soil solutions in nature are always in contact with solid phases. If chemical equilibrium is assumed to exist between a soil solution and its associated solids, then important information about the solubilities of the solution components can be obtained through a calculation performed by GEOCHEM. There are three principal kinds of problems in solubility equilibria that the program can resolve:

a. Supersaturation in a metal or a ligand with respect to the most stable solid phase possible. For example, analytical data for a saturation extract taken from a calcareous soil could be checked for supersaturation in Ca with respect to $CaCO_3(s)$ in the form of calcite, or data for an acid soil could be checked for supersaturation in Al with respect to $Al(OH)_3(s)$ in the form of gibbsite.

b. Precipitation or dissolution caused by the addition of a solid mixture to a soil solution. Important examples of this kind of chemical problem include the precipitation of salts or dissolution of solids induced by the application of manure, sewage sludge, or chemical fertilizer to a soil. The metal cations and the ligands (including HCO_3^- from organic matter decomposition) in an applied manure may react with the constituents of a soil solution to produce new solid phases or add to existing ones. On the other hand, the added ligands may react with metal cations already present to induce the further dissolution of an existing solid.

c. Precipitation or dissolution caused by the addition of an aqueous mixture to a soil solution. This kind of chemical problem occurs when, e.g., a soil is irrigated with water whose composition is significantly different from that of the soil solution; or a wastewater from some industrial process or agricultural operation is spilled accidentally or disposed of on land; or a geothermal brine leaks through the bottom liner of a storage lagoon and into the soil below.

Table 14 lists some analytical data pertaining to a simple situation having features common to both types a and b mentioned above. Except for Cd, the data are for a saturation extract of Holtville soil (Typic Torrifluvent), which is calcareous. In this case it is desired to find out if $CdSO_4$ added to the Holtville soil to produce a total concentra-

tion of 10^{-6} M Cd in the saturation extract would cause the precipitation of Cd entirely as $CdCO_3(s)$ and, if this occurred, what would be the concentration of water-soluble Cd remaining.

The computation on GEOCHEM is set up in this case by making only a single modification in the card deck arrangement that was described in section 2. In columns 10-12 of Card No. 1, a "0" is inserted, meaning "solids may precipitate, but none is imposed". This "0" replaces the "-1" used previously when no solid phases were permitted. In this particular case, a "0" is retained in columns 25-27 of Card No. 1, indicating that no mixed solid is to be considered.

Table 15 shows the output from the subroutine OUTCST for the system described in Table 14. There are 51 possible soluble complexes and 10 possible solids that could form from reactions among the components, according to the thermodynamic data in the program. Under the heading "SOLID", the values of $10^2 \log {}^cK$ are given along with the stoichiometric indices for the 10 solids. The conditional equilibrium constant ${}^cK$ describes the reaction

$$\alpha M + \beta L + \gamma H = M_\alpha H_\gamma L_\beta (s) \qquad (8)$$

where all of the symbols have the same meaning as in Eq. (3), except that now a solid species is formed instead of a soluble complex. An equation analogous to Eq. (4) can be written for metal-hydroxy solids, also. The thermodynamic equilibrium constant for Eq. (8) is exactly analogous to K given by Eq. (6). Thus the thermodynamic K-values stored in GEOCHEM for solids are equal to the inverses of the usual solubility product constants that describe the reverse of the reaction in Eq. (8).

TABLE 14. ANALYTICAL DATA FOR A SATURATION EXTRACT OF HOLTVILLE SOIL

Element	pC*	Element	pC
Ca	2.28	Cd	6.00
Mg	2.64	CO_3	2.39
K	2.89	SO_4	2.12
Na	2.00	Cl	2.03

* pC = -log total molar concentration

TABLE 15. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEM DESCRIBED IN TABLE 14
(Constants Corrected to the Ionic Strength of the Solution when the Computations Converged)

INPUT DATA FOR VERIFICATION

MET	LIG	*	SOLID				*	COMPLEXES											
1	1	773	1 1 0	0	0 0 0	0	0 0 0	254	1 1 0	1078	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	2	393	1 1 0	0	0 0 0	0	0 0 0	164	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	3	0	0 0 0	0	0 0 0	0	0 0 0	22	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	99	-2315	1 0-2	0	0 0 0	0	0 0 0	-1271	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	1	443	1 1 0	653	5 4-2	0	0 0 0	224	1 1 0	1068	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	2	0	0 0 0	0	0 0 0	0	0 0 0	154	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	3	0	0 0 0	0	0 0 0	0	0 0 0	12	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	99	-1685	1 0-2	0	0 0 0	0	0 0 0	-1191	1 0-1	-3945	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	1	0	0 0 0	0	0 0 0	0	0 0 0	52	1 1 0	971	1 1 1	17	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	2	0	0 0 0	0	0 0 0	0	0 0 0	52	1 1 0	141	1 1 1	97	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	3	0	0 0 0	0	0 0 0	0	0 0 0	-35	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	99	0	0 0 0	0	0 0 0	0	0 0 0	-1447	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	1	77	2 1 0	0	0 0 0	0	0 0 0	22	1 1 0	1001	1 1 1	-106	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	2	0	0 0 0	0	0 0 0	0	0 0 0	72	1 1 0	151	1 1 1	97	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	3	0	0 0 0	0	0 0 0	0	0 0 0	-15	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	99	0	0 0 0	0	0 0 0	0	0 0 0	-1417	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
11	1	1133	1 1 0	0	0 0 0	0	0 0 0	304	1 1 0	513	1 2 0	603	1 3 0	1138	1 1 1	0	0 0 0	0	0 0 0
11	2	0	0 0 0	0	0 0 0	0	0 0 0	164	1 1 0	223	1 2 0	176	1 3 0	228	1 1 1	0	0 0 0	0	0 0 0
11	3	0	0 0 0	0	0 0 0	0	0 0 0	162	1 1 0	217	1 2 0	157	1 3 0	342	1 4 0	-877	1 1-1	0	0 0 0
11	99	-1385	1 0-2	0	0 0 0	0	0 0 0	-1021	1 0-1	-2055	1 0-2	-3335	1 0-3	-4715	1 0-4	-918	2 0-1	-3265	4 0-4
50	1	1775	0 1 2	0	0 0 0	0	0 0 0	996	0 1 1	1625	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	2	0	0 0 0	0	0 0 0	0	0 0 0	166	0 1 1	-858	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	3	0	0 0 0	0	0 0 0	0	0 0 0	-845	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	99	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0

Table 16 shows the output from the subroutine OUT 1. It may be seen that the system described by the data in Table 14 proved to be supersaturated in Ca and Cd relative to $CaCO_3(s)$ and $CdCO_3(s)$. Of the original 5.25×10^{-3} mol/liter Ca present in the system, 2.83×10^{-3} mol/liter finally precipitated as $CaCO_3(s)$. Of the original 10^{-6} mol/liter Cd, 1.94×10^{-7} mol/liter precipitated as $CdCO_3(s)$. The precipitation of $CaCO_3(s)$ would not be expected in a saturation extract at

TABLE 16. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 14

NUMBER OF ITERATIONS = 75

SOLID CD CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS = 76

NUMBER OF ITERATIONS = 79

NUMBER OF ITERATIONS = 81

IONIC STRENGTH = 3.0750133E-02

FIXED PH = 7.900 COMPUTED TOTH = 0.1247194E-02

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	1.8540472E-03	2.73188	5.2480847E-03	2.28000	-1.0710210E-08
MG	1.8487140E-03	2.73313	2.2908757E-03	2.64000	4.9348046E-09
K	1.2608315E-03	2.89934	1.2882538E-03	2.89000	4.2022830E-11
NA	9.6562132E-03	2.01519	1.0000009E-02	2.00000	-5.1958438E-11
CD	4.6571682E-07	6.33188	1.0000031E-06	6.00000	0.0
CO3-	1.0043404E-05	4.99812	4.0738136E-03	2.39000	5.3432814E-12
SO4	6.3173249E-03	2.19947	7.5857900E-03	2.12000	7.2656832E-09
CL	9.2811882E-03	2.03240	9.3325600E-03	2.03000	-2.0891839E-09

SOLID			MOLES PER LITER OF SOLUTION
CA	CO3-	1	2.8335829E-03
CD	CO3-	1	1.9441893E-07

equilibrium. It is possible that this precipitation occurs in the calculation by GEOCHEM because the value of CO_{3T} was determined on a sample of extracted solution immediately after its withdrawal and, therefore, that the value of CO_{3T} represents an equilibrium with a partial pressure of CO_2 that is relatively high. Since the calculation by GEOCHEM treated the system as closed with respect to CO_2, $CaCO_3(s)$ was "forced" to precipitate. More will be said about this point in section 6. Another possibility is that the data in Table 14 do not represent true equilibrium and the system is kinetically supersaturated with respect to $CaCO_3(s)$. A third possibility, of course, is that there is an experimental error in the analytical data.

Table 17 lists the output from the subroutine OUT138. The noteworthy point here is that, when solids are involved, OUT 138 prints the mole percentage distribution of both soluble and solid species for each metal and ligand. In order to know the percentage distribution of a component among soluble species alone, it would be necessary to divide each percent figure given for the free ionic and complexed forms by the difference between 1.00 and the percent in solid form/100. Insofar as the objective in analyzing the data in Table 14 is concerned, it is seen that, under the conditions of the calculation, 19.4% of the added Cd is predicted to precipitate as $CdCO_3(s)$.

The example discussed here is a simple prototype for any calculation by GEOCHEM relating to solubility equilibria in a soil solution, provided that no solid is assumed a priori to precipitate and no mixed solids are involved. If mixed solids must be included in the calculation, then two things must be done. First, of course, a "1" must be entered in columns 25-27 of Card No. 1, meaning "mixed solids are considered". Secondly, a new card must be inserted after Card No. 6 (the CO_2 partial pressure card):

Card No. 11. Format 20I4

This card is left entirely blank if all of the mixed solids being considered are simply allowed to precipitate. If some of the mixed solids considered are to be prevented from precipitating, then the following card format is employed.

Card Columns	Type of Information
1-4	Enter a minus sign, then the code number of a mixed solid that is not allowed to precipitate, taken from Table 1.3.
5-8, etc.	Repeat the procedure for a second mixed solid that must not precipitate, etc., up to 20.

TABLE 17. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE SYSTEM DESCRIBED IN TABLE 14

PRIMARY DISTRIBUTION OF METALS AND LIGANDS *

CA		
	AS A FREE METAL/	35.3 PERCENT
	BOUND WITH CO3-/	0.4 PERCENT
	IN SOLID FORM WITH CO3-/	54.0 PERCENT
	BOUND WITH SO4 /	9.7 PERCENT
	BOUND WITH CL /	0.5 PERCENT
MG		
	AS A FREE METAL/	80.7 PERCENT
	BOUND WITH CO3-/	0.6 PERCENT
	BOUND WITH SO4 /	17.7 PERCENT
	BOUND WITH CL /	1.0 PERCENT
K		
	AS A FREE METAL/	97.9 PERCENT
	BOUND WITH SO4 /	2.1 PERCENT
NA		
	AS A FREE METAL/	96.6 PERCENT
	BOUND WITH CO3-/	0.1 PERCENT
	BOUND WITH SO4 /	3.3 PERCENT
CD		
	AS A FREE METAL/	46.6 PERCENT
	BOUND WITH CO3-/	1.9 PERCENT
	IN SOLID FORM WITH CO3-/	19.4 PERCENT
	BOUND WITH SO4 /	13.2 PERCENT
	BOUND WITH CL /	18.7 PERCENT
	BOUND WITH OH /	0.2 PERCENT
CO3-		
	AS A FREE LIGAND/	0.2 PERCENT
	BOUND WITH CA /	0.5 PERCENT
	IN SOLID FORM WITH CA /	69.6 PERCENT
	BOUND WITH MG /	0.4 PERCENT
	BOUND WITH NA /	0.3 PERCENT
	BOUND WITH H /	29.0 PERCENT
SO4		
	AS A FREE LIGAND/	83.3 PERCENT
	BOUND WITH CA /	6.7 PERCENT
	BOUND WITH MG /	5.3 PERCENT
	BOUND WITH K /	0.3 PERCENT
	BOUND WITH NA	4.3 PERCENT
CL		
	AS A FREE LIGAND/	99.4 PERCENT
	BOUND WITH CA /	0.3 PERCENT
	BOUND WITH MG /	0.2 PERCENT

* NOTE: "BOUND WITH" means in complexed form and does not include solids.

For each mixed solid (up to 20) that must not precipitate, there must be an entry in Card No. 11. For each mixed solid that is allowed (but not imposed) there is no entry on the card. Regardless of whether Card No. 11 is blank or filled in, it must always be the last card in the input data deck, unless adsorption phenomena are also being considered.

When mixed solids are considered, their $10^2 \log^2 K$ values are printed as part of the output from OUTCST and they are treated the same as any other solid in the remainder of the output.

CALCULATIONS WITH IMPOSED AND/OR UNALLOWED SOLIDS

There are two important reasons for imposing and/or not allowing solids during a solubility equilibrium calculation performed by GEOCHEM:

a. If the system is known empirically to be supersaturated with respect to certain solid phases, then these solids can be "clamped" selectively during the calculation. The remaining solids that are possible may be allowed to precipitate or even be imposed.

b. If the solution under consideration is known empirically to be in equilibrium with one or more solid phases, or if one or more solids is expected with certainty to precipitate from the solution, these solids may be imposed on the calculation from the outset.

The possibility of not allowing certain solids in a calculation endows GEOCHEM with the flexibility to describe accurately systems that are not strictly in equilibrium with respect to solid phases. This situation could occur frequently in soil solutions.

If a solid is imposed for a calculation and actually does precipitate, according to the criteria for chemical equilibrium, a great deal of time may be saved in a computation for a large system. On the other hand, if the solid is imposed incorrectly, the computation will converge very slowly and may even be interrupted without convergence (see the Appendix). In general, a solid should be expected with a high degree of certainty before it is imposed.

Before a set of solids is imposed, it should be checked for conformity with the Gibbs phase rule. If too many solids are imposed, an error message will be generated (see the Appendix). The Gibbs phase rule states that the number of intensive variables* which can be varied independently in a chemical system, f, is given by the expression:

$$f = C + 2 - P \qquad (9)$$

*The intensive variables are temperature, pressure, and a chemical potential for each component in each phase.

where C is the number of components in the system and P is the number of phases. Since temperature and pressure are stipulated during a calculation by GEOCHEM, and since there is always an aqueous phase present, Eq. (9) may be reduced to

$$f_e = C - P_s \tag{10}$$

where P_s is the number of solid phases present and $f_e = f - 2 + P - P_s = f - 1$. The smallest value allowed for f_e is 1, because the smallest value for f is 2 if the temperature and pressure of the system always are to be stipulated at will. Now, a component is defined as a constituent whose mass can be varied independently in a closed chemical system. Therefore, in applying Eq. (10), C must be calculated by subtracting from the number of neutral compounds in the system the number of chemical reactions that are possible between those compounds (see, e.g., Guggenheim, 1967, pp. 33-34 and 265-267).

As an example, consider a closed system containing $CaCO_3$, $Ca(OH)_2$, H_2CO_3, and H_2O. Of these constituents, only three may be taken as components because of the chemical reaction

$$CaCO_3(aq) + 2H_2O = Ca(OH)_2(aq) + H_2CO_3(aq) \tag{11}$$

The maximum number of solid phases that can form in the system is, accordingly, the solution of Eq. (10) for $f_e = 1$, i.e., $1 = 3 - P_s(max)$, or $P_s(max) = 2$ solid phases. Thus, both $CaCO_3(s)$ and $Ca(OH)_2(s)$ could be imposed for this system with no violation of the Gibbs phase rule. On the other hand, in a system containing $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, H_2CO_3, and H_2O, the five solids $CaCO_3(s)$, $MgCO_3(s)$, $CaMg(CO_3)_2(s)$, $Ca(OH)_2(s)$, and $Mg_4(OH)_2(CO_{3e})_3(s)$ cannot all be imposed because there are four components in this system and $P_s(max) = 3$ according to Eq. (10) with $f_e = 1$.

In order to perform a calculation with GEOCHEM in which some solid phases are imposed and some are not allowed, three modifications must be made in the card deck arrangement that was described in section 2. First, in columns 10-12 of Card No. 1 the total number of solids imposed plus those not allowed to precipitate must be inserted. This number can be as large as 13. Also, in columns 25-27 of the same card, either a "0" or a "1" must be entered depending on whether mixed solids are to be considered, as discussed earlier in this section. Secondly, a new card must be inserted after Card No. 6:

Card No. 9. Format 39I2

Card Columns	Type of Information
1-2	Code number of the metal in a chosen solid

Card Columns	Type of Information
3-4	Code number of the ligand in a chosen solid
5-6	Enter "-1", "-2", or "-3" if the solid is not allowed, or "+1", "+2", or "+3", if it is imposed, according to the solid's number in the thermodynamic data file.
7-8, etc.	Repeat the procedure for each imposed or unallowed solid, up to 13.

A negative entry disallows the solid for all cases in the computation; a positive number imposes it for the first case only. The last modification to be made is the addition of the mixed solids card:

Card No. 11. Format 20I4

Card Columns	Type of Information
1-4	Enter the code number of a chosen mixed solid (Table 1) as a negative number, if the solid is not allowed, or as a positive number, if the solid is imposed.
5-8, etc.	Repeat the procedure for all imposed or unallowed mixed solids, up to 20.

Thermodynamic data for unallowed solids will not appear in the output from OUTCST. A listing of the imposed solids will be given as part of the output from OUT 1.

SECTION 4

REDOX EQUILIBRIA

There are two different ways in which the reactions of oxidized and reduced species in a soil solution can be described with the help of GEOCHEM:

a. If there is experimental evidence that two species coupled by a redox equation occur simultaneously in significant concentrations in a soil solution, then both species should be included in the calculation as input metals or ligands and no redox equation should be considered. For example, if both $NH_3(aq)$ (i.e., NH_4^+) and NO_3^- are expected in a system, then ligands 7 and 57 in the list in section 1 should be included in the calculation which then proceeds as described in sections 2 and 3. Similarly, if Fe^{3+} (SO_4^{2-}) is expected to represent virtually all of the free iron (sulfur) ions in a system, or if Fe^{2+} (S^{2-}) is expected to do the same, then one or the other of these metal (ligand) ions should be an input metal (ligand) in the calculation and the redox half-reaction between them should be ignored. In general, if experimental data indicate that redox equilibrium does not exist because of kinetic or biological factors, or that one member of a redox couple is completely dominant, redox equations should not be included as part of the calculation by GEOCHEM. Attempts to compute the concentration of a redox species which may be present in negligible concentrations at the pE value considered may lead to nonconvergence and system generated error messages.

b. If there is reason to believe that a redox half-reaction is actually occurring in a system (e.g., SO_4^{2-} reduction to S^{2-} in a waterlogged soil), then the reaction may be included as a part of the criteria for chemical equilibrium in a calculation performed by GEOCHEM.

In order to consider redox equilibria in a computation for a soil solution, several things must be done. First, a "1" must be entered in columns 22-24 of Card No. 1, meaning "redox reactions are considered". In addition, if the redox reactions bring in metals or ligands listed in Table 1.1 that are not already being specified as representing a total concentration value in the analytical data for the system, these metals or ligands must be included in the data entered into columns 1-3 and 4-6 of Card No. 1. Cards similar to Card No. 3A or 4A also must be included, with the total concentration for each case set equal to 10^{-8} M so as not to alter significantly the input analytical data. For

example, if the sulfur content of a soil solution is to be specified by the input total concentration of SO_4^{2-} and if redox reaction 8 in Table 2 is to be considered, then both SO_4^{2-} and S^{2-} must be accounted for in columns 4-6 of Card No. 1 and a ligand card for S^{2-} must be employed with each entry set equal to 8.0. For a given redox couple, the choice of which species to assign the total analytical concentration is, of course, arbitrary, as is the choice of which specie is to be the reactant and which the product in the half-reaction. Regardless of which species is assigned the total analytical concentration in the input data deck, GEOCHEM assigns the total concentration always to the species designated as the reactant in each redox half-reaction shown in Table 2. In the case of the SO_4^{2-}/S^{2-} couple, this is SO_4^{2-}; in the case of Fe^{3+}/Fe^{3+} it is also the oxidized species. However, for the Cu^{2+}/Cu^{+} couple the reduced species has been chosen, as it has also in the case of NH_3/NO_3^-. The method of assignment of total concentrations by GEOCHEM in the case of redox couples will be made clear in the examples to be discussed later in this section.

Next, an electron activity card must be included:

Card No. 7. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of pE = -log (electron activity) for the first case.
6-10, etc.	Repeat the procedure for each case considered.

The concept of pE has been discussed at length by Stumm and Morgan (1970, Chap. 7). The pE value plays a role in redox equilibria that is similar to the role played by the pH value in acid-base equilibria. The relation between pE and E_H, the redox potential, is given in the expression:

$$pE = \frac{E_H}{59.155} \qquad (12)$$

where E_H is measured in millivolts. If the value of E_H is known or can be estimated for a given soil solution, the pE value is calculated according to Eq. (12). For soils, pE can range from about -7.0 to +14.

If redox reactions are being considered and NO_3^- is one of the input ligands, then a N_2 partial pressure card must be added:

Card No. 8. Format F5.2

Card Columns	Type of Information
1-5	Enter "0" if the system is closed with respect to $N_2(g)$. (Enter -log P_{N_2} otherwise.)

In this section it will be assumed that the system is closed and, therefore, that Card No. 8 contains only a "0" in columns 1-5.

Finally, a redox reaction card must be included:

Card No. 10. Format 20I2

Card Columns	Type of Information
1-2	Enter the redox reaction number from Table 2.
3-4, etc.	Repeat the procedure for a second reaction, up to 20.

With the addition of Card Nos. 7 and 10 (as well as 8 when necessary), the computation is run similarly to what was discussed in sections 2 and 3. For purposes of calculation, redox reactions are classified into three categories in GEOCHEM. Type A reactions are those in which a complex is involved (e.g., Reaction No. 10 in Table 2). Type B reactions include a solid phase (e.g., No. 2 in Table 2), while Type C reactions relate only metals or ligands (e.g., Nos. 1 and 8 in Table 2). A given redox reaction is characterized by the parameters KRED, MREDOX, LREDOX, NELEC, NHRED, and REDCST. The values of these parameters depend on both the type and the number of the redox reaction, as indicated in Table 18. Numerical information concerning the parameters is printed as part of the output from the subroutine OUTCST.

Table 19 lists some analytical data for a saturation extract of an Altamont soil (Typic Chromoxerert) that has been amended with sewage sludge. Two examples of redox calculations involving these data will be given. In the first example, the objective is to discover whether significant concentrations of Fe(II) AND Cu(I) would exist in the Altamont soil solution when the redox potential is about +650 mV. Table 20 shows a portion of the output from the subroutine OUTCST and the complete output from the system description provided by GEOCHEM. The output from OUTCST gives the values of the six redox parameters for reactions 1 and 22 in Table 2. It may be noted that MREDOX and LREDOX are equal to 4 and 5, respectively, because Fe^{3+} and Fe^{2+} occupy the fourth and fifth positions in the list of input metals provided in the system description. For the same reason Cu^{+} and Cu^{2+} correspond to MREDOX = 10 and LREDOX = 7. NELEC is equal to -1 for reaction 1 and +1 for reaction 22 in Table 2 because of the way those reactions are written in the table. REDCST is equal to $10^{2}\log^{c}K$, with log K as given in Table 2. Table 21 shows the output from the subroutine OUT 1. Note that the initial total concentration of Cu^{2+} is listed as 0.0 even though Table 20 shows that it was entered as $10^{-5.72}$ M. Because Cu^{+} is the reactant species in reaction 22 it is assigned the total input concentration of Cu by GEOCHEM. The objective in doing this example is met in Table 22, which shows part of the output from the subroutine OUTMAT. It may be seen that both Fe(II) and Cu(I) are insignificant in the system at pE = 11.

As a second example, the effect of lowering the redox potential to about -120 mV on the trace metals Cd, Cu, and Zn, in regard to sulfide precipitation, may be considered. Table 23 shows part of the output from OUTCST along with the system description for this problem. Table 24 gives the output from OUT1, which shows that essentially all of the Cd, Cu, and Zn present would precipitate as sulfides if the pE were to drop to -2. (It also turns out that the solution is supersaturated with respect to hydroxy apatite.) In a more realistic simulation, redox reactions involving Cu, Fe, Mn, and NO_3 also would be considered.

TABLE 18. PARAMETERS CHARACTERIZING A REDOX HALF-REACTION IN GEOCHEM

Reaction Type	KRED	MRED	LRED
A	Complex No.*	Metal No.≠	Ligand No.#
B	Minus Solid No.†	Metal No.	Ligand No.
C	-10 if 2 metals	Metal No.	Metal No.**
C	+ 10 if 2 ligands	Ligand No.§	Ligand No.

NELEC = stoichiometric coefficient of e^- in the redox reation in Table 2

NHRED = stoichiometric coefficient of H^+ in the redox reaction in Table 2

REDCST = $10^2 \log^c K$ (log K from Table 2)

* The number assigned to the complex in the thermodynamic data file (see Section 8).

† Minus the number assigned to the solid in the thermodynamic data file (see Section 8).

≠ Numerical position of the reactant metal in the input list of metals.

§ Numerical position of the reactant ligand in the input list of ligands.

\# Numerical position of the product ligand in the input list of ligands.

** Numerical position of the product metal in the input list of metals.

TABLE 19. ANALYTIC DATA FOR A SATURATION EXTRACT OF ALTAMONT SOIL

Component	pC	Component	pC
Ca	2.07	CIT	4.14
K	3.70	SAL	4.27
Na	3.00	PHTH	3.97
Fe	4.75	ARG	4.49
Mn	4.70	ORN	4.36
Cu	5.72	LYS	4.36
Cd	5.85	VAL	4.36
Zn	5.13	NO_3	2.17
CO_3	2.70	MAL	3.97
SO_4	2.70	BES	4.27
Cl	2.28	pH = 6.30	
PO_4	4.00		

TABLE 20. OUTPUT FROM OUTCST FOR REDOX DATA AND DESCRIPTION OF A SYSTEM BASED ON THE ANALYTICAL DATA IN TABLE 19
(Constants corrected for ionic strength at convergence)

50	57	0	0	0	0	0	0	0	0	0	0	0	0	-148	0	1	1	0	0	0	0
50	60	0	0	0	0	0	0	0	0	0	0	0	0	596	0	1	1	776	0	1	2
50	61	0	0	0	0	0	0	0	0	0	0	0	0	59	0	1	1	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

REDOX DATA	KRED	MREDOX	LREDOX	NELEC	NHRED	REDCST
	-10	4	5	-1	0	1266
	-10	10	7	1	0	-239

THESE COMPUTATIONS INVOLVE 11 METALS, 15 LIGANDS, 294 COMPLEXES AND 28 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	LIGAND	#INMAT	GUESS	TOTCC 1
CA	1	4.000	2.070	CO3-	1	2.700	2.700
K	4	5.000	3.700	SO4	2	4.000	2.700
NA	5	4.500	3.000	CL	3	4.000	2.280
FE3	6	6.000	4.750	PO4	9	5.000	4.000
FE2	7	8.000	8.000	CIT	17	5.000	4.140
MN	8	6.000	4.700	SAL	19	5.000	4.270
CU2+	9	7.000	5.720	PHTH	32	5.000	3.970
CD	11	6.000	5.850	ARG	33	5.000	4.490
ZN	12	6.500	5.130	ORN	34	5.000	4.360
CU1+	33	8.000	8.000	LYS+	35	5.000	4.360
				VAL	42	5.000	4.360
				NO3	57	3.500	2.170
				MAL	60	5.000	3.970
				BES	61	6.000	4.270

FIXED PH 6.300

REDOX POTENTIAL 11.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE2/FE3
CU1/CU2

TABLE 21. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 20

CASE NUMBER 1

NUMBER OF ITERATIONS = 35

NUMBER OF ITERATIONS = 39

NUMBER OF ITERATIONS = 41

IONIC STRENGTH = 2.5065232E-02

FIXED PH = 6.300 COMPUTED TOTH = 0.3510528E-02

PE = 11.00

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.4936673E-03	2.12531	8.5114017E-03	2.07000	4.7293238E-08
K	1.9722481E-04	3.70504	1.9952665E-04	3.70000	-6.2012340E-12
NA	9.8530855E-04	3.00643	1.0000013E-03	3.00000	-1.5822928E-10
FE3	1.2622536E-15	14.89886	1.7792830E-05	4.74975	-9.5781694E-10
FE2	5.7695222E-14	13.23886	0.0	*******	-9.5781694E-10
MN	1.7083759E-05	4.76742	1.9952669E-05	4.70000	1.8985349E-10
CU2+	6.2693495E-09	8.20278	0.0	*******	1.4824764E-10
CD	9.0309078E-07	6.04427	1.4125435E-06	5.85000	4.9427532E-11
ZN	4.9611926E-06	5.30441	7.4131376E-06	5.13000	4.0435788E-10
CU1+	1.5389755E-17	16.81277	1.9154695E-06	5.71772	1.4824764E-10
CO3-	1.6787618E-07	6.77501	1.9952657E-03	2.70000	1.2340024E-08
SO4	1.3951729E-03	2.85537	1.9952657E-03	2.70000	2.5260210E-08
CL	5.1634870E-03	2.28706	5.2480847E-03	2.28000	-1.1897628E-09
PO4	3.0834099E-11	10.51097	1.0000018E-04	4.00000	4.7903086E-09
CIT	2.8663648E-17	16.54266	7.2443858E-05	4.14000	4.8418336E-09
SAL	1.8150490E-12	11.74111	5.3703363E-05	4.27000	7.3896445E-11
PHTH	4.9751121E-05	4.30320	1.0715231E-04	3.97000	3.7772487E-09
ARG	4.1592465E-08	7.38099	3.2359472E-05	4.49000	6.6774586E-11
ORN	5.3540028E-12	11.27132	4.3651729E-05	4.36000	-1.1260681E-10
LYS	2.6873365E-12	11.57068	4.3651729E-05	4.36000	-2.6060065E-10
VAL	2.2356282E-08	7.65060	4.3651729E-05	4.36000	-7.4152240E-11
NO3	6.6271834E-03	2.17867	6.7608543E-03	2.17000	-2.4118652E-09
MAL	5.3814671E-05	4.26910	1.0715231E-04	3.97000	1.6364368E-09
BES	4.9778537E-05	4.30296	5.3703363E-05	4.27000	2.0190100E-12

TABLE 22. OUTPUT FROM THE SUBROUTINE OUTMAT FOR THE SYSTEM DESCRIBED IN TABLE 20

	FREE MET	CO3-	SO4	CL	PO4	CIT	SAL	PHTH	ARG	ORN	LYS
FREE LIG		6.78	2.86	2.29	10.51	16.54	11.74	4.30	7.38	11.27	11.57
CA	2.13	4.31	3.23	4.09	4.58	4.26	5.88	4.28	****	****	****
K	3.71	6.96	5.94	6.41	7.51	****	****	****	****	****	****
NA	3.01	5.96	5.04	5.51	6.76	****	****	****	****	****	****
FE3	14.90	5.47	14.55	12.93	8.40	4.84	8.63	****	13.18	17.07	****
FE2	13.24	13.81	14.44	15.88	14.72	13.18	17.83	****	17.10	21.19	19.99
MN	4.77	6.04	5.87	7.40	6.55	7.10	10.06	****	9.83	14.32	13.92
CU2+	8.20	7.18	9.21	10.37	9.61	5.75	8.79	8.86	7.69	12.35	17.35
CD	6.04	7.72	7.15	6.60	8.69	7.18	11.64	7.20	9.91	13.40	12.09
ZN	5.30	5.79	6.31	8.03	7.32	9.45	9.60	6.86	8.27	12.26	20.46
CU1+	16.81	****	****	16.03	****	****	****	****	****	****	****
HYDROGEN	6.30	2.71	7.40	17.07	4.14	6.18	4.28	5.34	4.49	4.36	4.36

TABLE 23. OUTPUT FROM OUTCST FOR REDOX DATA AND DESCRIPTION OF A SYSTEM BASED ON THE ANALYTICAL DATA IN TABLE 19

50	57	0	0	0	0	0	0	0	0	0	0	0	0	-144	0	1	1	0	0	0	0
50	60	0	0	0	0	0	0	0	0	0	0	0	0	608	0	1	1	793	0	1	2
50	61	0	0	0	0	0	0	0	0	0	0	0	0	65	0	1	1	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

REDOX DATA	KRED	MREDOX	LREDOX	NELEC	NHRED	REDCST
	10	2	4	-8	8	1986

THESE COMPUTATIONS INVOLVE 9 METALS, 16 LIGANDS, 261 COMPLEXES AND 27 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	LIGAND	#INMAT	GUESS	TOTCC 1
CA	1	4.000	2.070	CO3-	1	2.700	2.700
K	4	5.000	3.700	SO4	2	4.000	2.700
NA	5	4.500	3.000	CL	3	4.000	2.280
FE3	6	6.000	4.750	S	8	8.000	8.000
MN	8	6.000	4.700	PO4	9	5.000	4.000
CU2+	9	7.000	5.720	CIT	17	5.000	4.140
CD	11	6.000	5.850	SAL	19	5.000	4.270
ZN	12	6.500	5.130	PHTH	32	5.000	3.970
				ARG	33	5.000	4.490
				ORN	34	5.000	4.360
				LYS	35	5.000	4.360
				VAL	42	5.000	4.360
				NO3	57	3.500	2.170
				MAL	60	5.000	3.970
				BES	61	6.000	4.270

FIXED PH 6.300

REDOX POTENTIAL -2.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

SO4/S-2

TABLE 24. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 23

CASE NUMBER 1

NUMBER OF ITERATIONS = 35

SOLID CU2+ S 1 PRECIPITATES

NUMBER OF ITERATIONS = 38

SOLID CA PO4 1 PRECIPITATES

NUMBER OF ITERATIONS = 41

SOLID CD S 1 PRECIPITATES

NUMBER OF ITERATIONS = 43

SOLID ZN S 1 PRECIPITATES

NUMBER OF ITERATIONS = 45

NUMBER OF ITERATIONS = 49

NUMBER OF ITERATIONS = 52

IONIC STRENGTH = 2.4808746E-02

FIXED PH = 6.300 COMPUTED TOTH = 0.3401679E-02

PE = -2.00

(Continued)

TABLE 24 (Continued)

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.3698163E-03	2.13254	8.5114017E-03	2.07000	-1.4697434E-09
K	1.9725425E-04	3.70497	1.9952665E-04	3.70000	-5.2346781E-12
NA	9.8547339E-04	3.00636	1.0000013E-03	3.00000	-8.0920243E-11
FE3	1.2128957E-15	14.91618	1.7782833E-05	4.75000	-3.2991432E-10
MN	1.7315775E-05	4.76156	1.9952669E-05	4.70000	-1.3001514E-11
CU2+	5.9628671E-18	17.22455	1.9054696E-06	5.72000	0.0
CD	1.4978361E-09	8.82454	1.4125435E-06	5.85000	0.0
ZN	1.4978292E-07	6.82454	7.4131376E-06	5.13000	0.0
CO3-	1.6811254E-07	6.77440	1.9952657E-03	2.70000	-1.3969839E-09
SO4	1.3949776E-03	2.85543	1.9952755E-03	2.70000	4.9658411E-10
CL	5.1650554E-03	2.28692	5.2480847E-03	2.28000	-3.4835639E-09
S	2.9144625E-18	17.53545	1.0506857E-05*	4.97853	4.9658411E-10
PO4	7.4286025E-13	12.12910	1.0000018E-04	4.00000	-1.4551915E-11
CIT	3.0047713E-17	16.52219	7.2443858E-05	4.14000	-1.0767214E-09
SAL	1.8158660E-12	11.74092	5.3703363E-05	4.27000	-1.3515944E-10
PHTH	5.0251023E-05	4.29886	1.0715231E-04	3.97000	-9.1784136E-11
ARG	4.1630070E-08	7.38059	3.2359472E-05	4.49000	3.5976666E-10
ORN	5.3539898E-12	11.27132	4.3651729E-05	4.36000	-1.1260681E-10
LYS	2.6873521E-12	11.57067	4.3651729E-05	4.36000	3.9426662E-10
VAL	2.2372259E-08	7.65029	4.3651729E-05	4.36000	3.1747049E-11
NO3	6.6293441E-03	2.17853	6.7608543E-03	2.17000	-1.4451293E-09
MAL	5.4094795E-05	4.26684	1.0715231E-04	3.97000	2.5220270E-11
BES	4.9842391E-05	4.30240	5.3703363E-05	4.27000	-6.6459338E-12

SOLID			MOLES PER LITER OF SOLUTION
CA	PO4	1	3.2534183E-05
CU2+	S	1	1.9054696E-06
CD	S	1	1.4101897E-06
ZN	S	1	7.1905833E-06

* Equal to the sum of concentrations of CdS, CuS, and ZnS.

SECTION 5

ADSORPTION AND EXCHANGE EQUILIBRIA

MODELS OF SURFACE CHEMICAL PHENOMENA IN GEOCHEM

The present state of understanding of surface chemical reactions in soils from the thermodynamic point of view is not nearly so advanced as in the cases of complexation, precipitation, and redox reactions. Currently, the surface behavior of cations and anions in soils is divided into two gross categories, adsorption and exchange, according to whether the surface reaction is considered to be largely irreversible or largely reversible, even though it is known that all adsorption processes involve the exchange of surface species and that many exchange processes are at least partly irreversible. As a general rule, adsorption phenomena tend to occur when relatively small concentrations of cations or anions interact with constant-potential surfaces and exchange phenomena tend to occur when ions interact with constant-charge surfaces (Sposito, 1977; Stumm and Morgan, 1970). These generalizations are strictly empirical guides with many exceptions (e.g., ion exchange occurs on kaolinite which has only constant-potential surfaces and adsorption can occur on the constant-charge surfaces of smectites). The classification of a particular soil surface reaction as adsorption or exchange is still a matter for individual discretion.

On a fundamental level, both adsorption and exchange processes concern the reactions of surface functional groups with ions and neutral molecules. Adsorption processes usually are those in which the functional groups display a very pronounced selectivity for one or more chemical species during a competitive exchange reaction. This selectivity can be expected to appear because the chemical bonds involved are more than simple interactions based on electrostatic or van der Waals forces. On the other hand, when the interactions do primarily involve the charge and size characteristics of the reacting species, selectivities are less pronounced and the surface process should exhibit the reversibility feature associated with exchange phenomena.

Not enough is known about the surface functional groups and the nature of surface chemical bonds in soils to develop a comprehensive thermodynamic picture of adsorption and exchange reactions. Accordingly, the description of these reactions currently accepted is empirical and includes assumptions whose fundamental basis and degree of generality have not yet been established. This fact should be appreciated thoroughly when employing the two surface reaction models that are available in

GEOCHEM. The characteristics of the particular problem the user of the program wishes to investigate should be examined carefully to delineate the possible limitations of the numerical results provided by GEOCHEM. In some cases the computations done by the program will be only of qualitative value and in others they may even be inappropriate.

CATION ADSORPTION PHENOMENA

GEOCHEM does not include a subroutine for anion adsorption, although provision for one has been made in columns 13-15 of Card No. 1. Cation adsorption reactions, e.g., the "specific adsorption" of Cu^{2+} by oxide surfaces, are described according to the semi-empirical model developed by James and Healy (1972). This paper should be read carefully before employing the program in a model calculation. (See also James et al., 1975, for some critical discussion of the model.) The James-Healy theory assumes that the total amount of metal adsorbed by a constant potential surface is the sum of the amounts of free metal cation and of all its known hydrolytic species on the surface. Each surface specie is considered to be in equilibrium with all other surface species and with the metal ions in solution, the equilibrium being governed by a conditional equilibrium constant that depends on the electrostatic, solvation, and non-coulombic interactions that occur. The data necessary in order to apply the model are the pH value at the point of zero charge (PZC) dielectric constant, and total area of the adsorbing surface as well as the contribution to the Gibbs free energy of adsorption from non-coulombic interactions. The PZC and area of the adsorbing surface can be determined experimentally by standard means (Stumm and Morgan, 1970). Typical estimates for the dielectric constant and the "chemical" part of the free energy of adsorption are $\epsilon = 4.3$ and $\Delta G_{chem} = -12RT$, where R is the gas constant in kcal/mol ^{o}K, T is the absolute temperature in ^{o}K, and ΔG_{chem} is expressed in kcal/mol (James and Healy, 1972).

To include cation adsorption in a calculation performed by GEOCHEM, the number of different adsorbing surfaces (up to 5) is entered in columns 16-18 of Card No. 1 and three additional data cards are prepared.

Card No. 12. Format 5F10.5.

Card Columns	Type of Information
1-10	Enter the value of RT/F = 0.0252 J/C at 25°C
11-20	Enter the value of $eF/16\pi\epsilon_o RT$ = 140 A..
21-30	Enter the radius of H_2O = 1.38 Å..
31-40	Enter the dielectric constant of $H_2O(l)$ = 78.5 at 25°C.
41-50	Enter "1.0" (James-Healy "z" parameter)

The data entered on Card No. 12 are the values of parameters in the James-Healy model. R and T have their usual meanings; F is the Faraday constant, ϵ_o is the permitivity of vacuum, and e is the protonic charge. The paper of James and Healy (1972) should be consulted for details.

Card No. 13. Format 2I2, 13F5.2.

Card Columns	Type of Information
1-2	Code number of adsorbing surface (90-94)
3-4	Enter the total number of adsorbing metals.
5-9	Enter PZC value for the surface.
10-14	Enter dielectric constant of the surface.
15-19	Enter a guess for -log "free" (i.e., without metal ions) adsorbing surface area in $10^4 m^2$/liter.
20-24	Enter -log total adsorbing surface area (for #90), in $10^4 m^2$/liter, for the first case.
25-29, etc.	Enter the same thing (for #90) for the second case, etc., up to 10 cases.

Card No. 13 is repeated for each different adsorbing surface, up to 5. The data entered in columns 15-19 are analogous to the estimate of free ionic concentration required in Card No. 4. The code numbers for adsorbing surfaces are listed in Section 1.

Card No. 14. Format 10(I2, F6.2).

Card Columns	Type of Information
1-2	Enter the code number of the first adsorbing metal (Section 1).
3-8	Enter the value of $\Delta G_{chem}/RT$ for the first adsorbing metal.
9-10, etc.	Repeat with data for the second
11-16, etc.	adsorbing metal, up to 10 metals.

The code numbers for all of the metals on Card Nos. 3A, 3B, etc., must be entered on Card No. 14 in increasing numerical order (i.e., their order in the list in Section 1). For each different adsorbing surface, a Card No. 14 is included directly after Card No. 13 for that surface. Some representative values of $\Delta G_{chem}/RT$ are given in Table I of the paper of James and Healy (1972).

CATION EXCHANGE EQUILIBRIA

The exchange equilibrium model in GEOCHEM applies only to mono- and bivalent cations interacting with a montmorillonite surface. The thermodynamic data stored in the program refer to two representative clay minerals, Camp Berteau montmorillonite and Chambers bentonite. The Camp Berteau clay is an example of a smectite without isomorphous substitutions in the tetrahedral sheet whereas the Chambers bentonite has substitutions in both the tetrahedral and octahedral sheets. Some chemical data relating to these minerals is given in Table 25.

TABLE 25. CHEMICAL FORMULAS, FORMULA WEIGHTS, AND FORMATION CONSTANTS OF THE HOMOIONIC MONTMORILLONITES CONSIDERED IN GEOCHEM

Camp Berteau

$X^{-1} = [(Al_{4.358}Fe^{3+}_{0.612}Fe^{2+}_{0.045}Mg_{0.955})Si_{11.94}O_{29.85}(OH)_{5.97}]^{-1}$

Formula	Formula wt.	log K_M	Formula	Formula wt.	log K_M
NaX	1114.94	0	CuX_2	2247.44	11.61
KX	1131.05	1.41	ZnX_2	2249.27	8.27
MgX_2	2208.22	1.81	CdX_2	2296.30	10.67
CaX_2	2223.98	2.12	PbX_2	2391.09	21.09
NiX_2	2242.61	6.52			

Chambers

$X^{-1} = [(Al_{2.891}Fe^{3+}_{0.467}Fe^{2+}_{0.016}Mg_{1.163})(Si_{8.304}Al_{0.391})O_{21.739}(OH)_{4.348}]^{-1}$

NaX	821.77	0	CuX_2	1661.10	13.26
KX	837.88	1.04	ZnX_2	1662.93	9.85
MgX_2	1621.87	3.51	CdX_2	1709.96	11.95
CaX_2	1637.64	3.37	PbX_2	1804.75	22.01
NiX_2	1656.27	8.18			

The cation exchange model has been described by Mattigod and Sposito (1979). It is based on three assumptions:

(1) The standard free energy of the reactions:

$$HX(s,aq) = H^{+}(sq) + X^{-1}(s,aq) \quad (13)$$

$$NaX(s,aq) = Na^{+}(aq) + X^{-1}(s,aq) \quad (14)$$

is equal to zero, where (s,aq) denotes a homoionic montmorillonite or its anionic part in equilibrium with an aqueous electrolyte solution and X refers to one equivalent of the anionic part of the montmorillonite (see Table 25). This assumption implies that H- and Na-montmorillonite will be completely dissociated when they are in equilibrium with an infinitely dilute solution. It may be noted that Eq. (13) and (14) are analogous to the dissolution reaction of a solid and that the equilibrium constants for the reactions are analogous to solubility product constants.

(2) The standard free energy of formation of Na-montmorillonite may be calculated by the correlation technique of Mattigod and Sposito (1978).

(3) The activity coefficients of MX_m (M = metal cation of valence m) in a mixture of homoionic montmorillonites are always unity.

Assumptions (1) and (2) are sufficient to permit the computation of exchange equilibrium constants, since every exchange reaction can be written as a combination of two reactions like

$$m\ NaX(s,aq) + M^{+m}(aq) = MX_m(s,aq) + m\ Na^{+}(aq) \quad (15)$$

with

$$\log K_{ex} = \frac{1}{5.708}\left[m\mu^{\circ}(NaX) + \mu^{\circ}(M^{+m}) - \mu^{\circ}(MX_m) - m\,\mu^{\circ}(Na^{+})\right] \quad (16)$$

at 25°C where μ° is a standard free energy of formation in kJ/mol (Mattigod and Sposito, 1979). Assumption (3) states that homoionic clays will "precipitate" as independent solid phases, just as, e.g., $CaCO_3(s)$ and $AlPO_4(s)$ would be expected to do (and are assumed to do in GEOCHEM). There is experimental evidence supporting this assumption for Na^{+}-bivalent and bivalent-bivalent exchanges, but not for exchanges involving K^{+}. There are no data available that pertain to the multication exchanges (e.g., Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} simultaneously) that are typical in natural soil solutions.

Assumptions (1) to (3) make it possible to regard cation exchange as a kind of precipitation-dissolution reaction. Accordingly, the homoionic montmorillonite MX_m is treated the same as an ordinary solid in GEOCHEM, in that formation constants for $MX_m(s,aq)$ are stored in the program (see Table 25) and X (either Camp Berteau or Chambers) is regarded as a solid-forming ligand. However, X (= CBER or CHAM) is assigned zero charge in GEOCHEM in order that it not contribute to the calculated ionic strength nor receive an activity coefficient computed according to the Davies equation.

In order to include cation exchange in a computation performed by GEOCHEM, one need only enter a total concentration of CBER or CHAM (in mol/liter) on a ligand card as described for ordinary solids in section 3. A corresponding set of total metal concentrations should also be entered on the appropriate cards in order to maintain electrical neutrality. The procedure may be understood by studying the following example computation.

AN EXAMPLE: ADSORPTION AND EXCHANGE OF Cd IN AN ACID, MONTMORILLONITIC SOIL.

Table 26 lists analytical data needed by GEOCHEM in order to predict the fate of $CdSO_4$ added to make a concentration of 10^{-6} M in the aqueous phase of a water-saturated San Miguel soil (Typic Natrixeralf, coarse-loamy, montmorillonitic, thermic). The Camp Berteau montmorillonite was chosen as a model for the clay fraction in this soil, insofar as cation exchange is concerned.

The total concentration of montmorillonite anion may be calculated from the expression:

$$MONT_T = CEC/S \qquad (MONT_T \text{ in mol/liter}) \tag{17}$$

where CEC is the cation exchange capacity of the soil in meq/gm soil and S is the gravimetric water content of the soil at saturation. The assumptions underlying Eq. (17) are that the clay fraction is entirely montmorillonite and accounts for all the cation exchange capacity of the soil and that the analytical data to be used as input to the program refer to a saturation extract. An additional, tacit assumption is that the aqueous phase which resides in the volume occupied by the whole soil is in contact with all of the clay fraction of that volume. In the case of the San Miguel soil, CEC = 0.177 meq/gm soil and S = 0.27 gm H_2O/gm soil, so $MONT_T$ = 0.66 M. One-half of this concentration was assigned each to the Ca and Mg forms of the clay, as indicated in Table 26.

The total area of adsorbing surface may be estimated using the equation:

$$A_T = Sp \times \% \text{ adsorbent} \times 10/S \qquad (A_T \text{ in } m^2/\text{liter}) \tag{18}$$

TABLE 26. ANALYTICAL DATA FOR A SAN MIGUEL SOIL SOLUTION

Component	pC	Component	pC
Ca	0.78*(2.58)	CO_3	3.70
Mg	0.78*(2.61)	SO_4	2.30
K	3.10	Cl	2.39
Na	2.52	CBER	0.18
Cd	6.00	pH	5.60

* Due to assignment of one-half $MONT_T$ to CaX_2 or MgX_2, where X = CBER: $MONT_T = 2\ CaX_2 + 2\ MgX_2 = 0.66$ M.

where Sp is the specific surface of the adsorbent in m^2/gm and % adsorbent is its weight percentage in the soil. In the present example, the product Sp x % adsorbent was taken equal to 12.1 m^2/gm soil. The PZC and dielectric constant of the adsorbent were set at 2.0 and 4.3, respectively. The values chosen for $\Delta G_{chem}/RT$ were -0.1 (Na), -0.1(K), -8(Mg), -10(Ca), and -12(Cd).

Table 27 shows the output from the subroutine OUTCST for this problem. The data entered on Card No. 12 are listed under the heading "Adsorption Data" along with the chosen values of PZC and the adsorbent dielectric constant. The formation constants (at ionic strength 0.0201 M) for the solids Ca-, Mg-, Na-, K-, Cd-, and H-montmorillonite are listed under "solid" in the usual way. Table 28 shows the output for the subroutine OUT 1. In this computation, all solids were allowed and the ionic strength was fixed at the value computed by GEOCHEM for the San Miguel soil solution in the absence of exchangeable cations and adsorbing surfaces. The values of pC for Ca and Mg in this reference soil solution are given in parentheses in Table 25. By employing the reference ionic strength, one is assuming that only solution species contribute to the ionic strength; the exchangeable cations are excluded. Table 28 gives the values of $2.303\Delta G_{ads}/RT$ and its component free energies for each metal and metal hydrolytic species that can be adsorbed (see James and Healy, 1972, for details concerning ΔG_{coul}, ΔG_{solv}, and ΔG_{chem}). Table 29 shows the output from OUT138. It

TABLE 27. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE ANALYTICAL DATA IN TABLE 26

ADSORPTION DATA

XRTF = 0.02520
XENPI = 140.00000
Rh = 1.38000
EPSBUL = 78.50000
ZEL = 1.00000

SURFACE	PZC	EPSOL
90	2.00	4.30

INPUT DATA FOR VERIFICATION

MET	LIG	* SOLID						* COMPLEXES											
1	1	791	1 1 0	0	0 0 0	0	0 0 0	271	1 1 0	1094	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	2	411	1 1 0	0	0 0 0	0	0 0 0	181	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	3	0	0 0 0	0	0 0 0	0	0 0 0	35	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	63	186	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	-9	126-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	99	-2318	1 0-2	0	0 0 0	0	0 0 0	-1275	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	1	461	1 1 0	699	5 4-2	0	0 0 0	241	1 1 0	1084	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	2	0	0 0 0	0	0 0 0	0	0 0 0	171	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	3	0	0 0 0	0	0 0 0	0	0 0 0	25	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	63	156	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	90	0	0 0 0	0	0 0 0	0	0 0 0	4	122 0	-10	122-1	16	422-4	0	0 0 0	0	0 0 0	0	0 0 0
2	99	-1688	1 0-2	0	0 0 0	0	0 0 0	-1195	1 0-1	-3957	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	1	0	0 0 0	0	0 0 0	0	0 0 0	65	1 1 0	986	1 1 1	33	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	2	0	0 0 0	0	0 0 0	0	0 0 0	65	1 1 0	156	1 1 1	113	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
4	3	0	0 0 0	0	0 0 0	0	0 0 0	-42	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	63	134	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	90	0	0 0 0	0	0 0 0	0	0 0 0	6	131 0	3	131-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	99	0	0 0 0	0	0 0 0	0	0 0 0	-1453	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	1	93	2 1 0	0	0 0 0	0	0 0 0	35	1 1 0	1016	1 1 1	-106	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	2	0	0 0 0	0	0 0 0	0	0 0 0	85	1 1 0	166	1 1 1	113	2 1 0	0	0 0 0	0	0 0 0	0	0 0 0
5	3	0	0 0 0	0	0 0 0	0	0 0 0	-22	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	63	-5	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	2	126-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	99	0	0 0 0	0	0 0 0	0	0 0 0	-1423	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
11	1	1151	1 1 0	0	0 0 0	0	0 0 0	361	1 1 0	411	1 2 0	1144	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0
11	2	0	0 0 0	0	0 0 0	0	0 0 0	181	1 1 0	241	1 2 0	190	1 3 0	244	1 1 1	0	0 0 0	0	0 0 0
11	3	0	0 0 0	0	0 0 0	0	0 0 0	175	1 1 0	223	1 2 0	203	1 3 0	145	1 4 0	-877	1 1-1	0	0 0 0
11	63	1046	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
11	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	-9	126-1	-13	126-2	-3	126-3	17	126-4	14	226-1
11	99	-1388	1 0-2	0	0 0 0	0	0 0 0	-1025	1 0-1	-2058	1 0-2	-3339	1 0-3	-4727	1 0-4	-930	2 0-1	-3277	4 0-4
50	1	1789	0 1 2	0	0 0 0	0	0 0 0	1008	0 1 1	1639	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	2	0	0 0 0	0	0 0 0	0	0 0 0	178	0 1 1	-860	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	3	0	0 0 0	0	0 0 0	0	0 0 0	-849	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	63	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	90	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	99	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0

TABLE 28. OUTPUT FROM OUT 1 FOR THE DATA DESCRIBED IN TABLE 26

ADSORPTION CONSTANTS

CONSTANTS FOR ADSORPTION ON SURFACE ADS1

METAL	LOGK (X100)						GCOUL						GSOLV						GCHEM
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	
CA	-29	-963	*****	*****	*****	*****	-9.1	-4.6	*****	*****	*****	*****	16.5	4.1	*****	*****	*****	*****	-10.0
MG	-165	-974	-6080	*****	*****	*****	-9.4	-4.7	-18.8	*****	*****	*****	18.1	4.5	72.5	*****	*****	*****	-8.0
NA	-117	-1598	*****	*****	*****	*****	-4.4	0.0	*****	*****	*****	*****	3.8	0.0	*****	*****	*****	*****	-0.1
K	-119	-1560	*****	*****	*****	*****	-4.6	0.0	*****	*****	*****	*****	4.2	0.0	*****	*****	*****	*****	-0.1
CD	54	-626	-1677	-3337	-5465	-1579	-9.1	-4.6	0.0	4.6	9.1	-13.7	16.6	4.2	0.0	4.2	16.6	37.4	-12.0

NUMBER OF ITERATIONS = 4

SOLID CD CBER 1 PRECIPITATES

NUMBER OF ITERATIONS = 76

SOLID CA CBER 1 PERCIPITATES

NUMBER OF ITERATIONS = 9

SOLID MG CBER 1 PRECIPITATES

NUMBER OF ITERATIONS = 12

IONIC STRENGTH = 2.0099998E-02

FIXED PH = 5.600 COMPUTED TOTH = 0.3384664E-03

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.1585715E-02	1.14517	1.6595882E-01	0.78000	0.0
MG	1.4283228E-01	0.84517	1.6595882E-01	0.78000	0.0
K	7.9090567E-04	3.10188	7.9433038E-04	3.10000	-8.0924531E-11
NA	3.0020922E-03	2.52258	3.0199585E-03	2.52000	-1.1300884E-10
CD	1.7981876E-10	9.74517	1.0000031E-06	6.00000	0.0
CO3-	8.8378727E-10	9.05365	1.9952665E-04	3.70000	-2.9103830E-11
SO4	3.8637361E-04	3.41299	5.0118901E-03	2.30000	2.8110065E-07
CL	2.8762678E-03	2.54117	4.0738136E-03	2.39000	3.7164256E-08
CBER	4.3912405E-01	0.35741	6.6069365E-01	0.18000	-1.1336995E-05
ADS1	2.1982737E-02	1.65792	4.4668481E-02	1.35000	4.4393590E-07

SOLID		MOLES PER LITER OF SOLUTION
CA	CBER	9.1305017E-02
MG	CBER	1.9473113E-02
CD	CBER	9.9977206E-07

may be noted that Cd is predicted to become entirely exchangeable, while Ca is partly adsorbed and partly exchangeable. The fact that about two-thirds of the added concentration of montmorillonite is predicted to be free ligand should be interpreted in the light of the log K values in Table 25. "Free ligand" means that the neutralizing cations are in the same state as Na^+ on Na-montmorillonite, since log K for that solid has been set equal to zero. If log K for Na-clay were chosen to be a positive quantity instead, then the values of log K for the bivalent exchangeable cations would be augmented by 2 log K_{Na} and a greater "precipitation" of Ca-, and Mg-montmorillonite would be predicted than what appears in Table 29.

TABLE 29. OUTPUT FROM OUT138 FOR THE DATA IN TABLE 26

PRIMARY DISTRIBUTION OF METALS AND LIGANDS *

```
CA
    AS A FREE METAL/   43.1 PERCENT
    BOUND WITH SO4-/    1.1 PERCENT
    BOUND WITH CL  /    0.3 PERCENT
    IN SOLID FORM WITH CBER/ 55.0 PERCENT
    BOUND WITH ADSI/    0.5 PERCENT
MG
    AS A FREE METAL/   86.1 PERCENT
    BOUND WITH SO4 /    1.7 PERCENT
    BOUND WITH CL  /    0.4 PERCENT
    IN SOLID FORM WITH CBER/ 11.7 PERCENT
K
    AS A FREE METAL/   99.6 PERCENT
    BOUND WITH SO4 /    0.2 PERCENT
    BOUND WITH CL  /    0.1 PERCENT
    BOUND WITH ADSI/    0.1 PERCENT
NA
    AS A FREE METAL/   99.4 PERCENT
    BOUND WITH SO4 /    0.3 PERCENT
    BOUND WITH CL  /    0.2 PERCENT
    BOUND WITH ADSI/    0.1 PERCENT
CD
    IN SOLID FORM WITH CBER/100.0 PERCENT
CO3-
    BOUND WITH CA  /    7.0 PERCENT
    BOUND WITH MG  /   11.0 PERCENT
    BOUND WITH H   /   82.0 PERCENT
SO4
    AS A FREE LIGAND/   7.7 PERCENT
    BOUND WITH CA  /   35.6 PERCENT
    BOUND WITH MG  /   56.5 PERCENT
    BOUND WITH NA       0.2 PERCENT
CL
    AS A FREE LIGAND/  70.6 PERCENT
    BOUND WITH CA  /   11.3 PERCENT
    BOUND WITH MG  /   17.9 PERCENT
    BOUND WITH NA  /    0.1 PERCENT
CBER
    AS A FREE LIGAND/  66.5 PERCENT
    IN SOLID FORM WITH CA  / 27.6 PERCENT
    IN SOLID FORM WITH MG  /  5.9 PERCENT
ADSI-
    AS A FREE LIGAND/  49.2 PERCENT
    BOUND WITH CA  /   47.0 PERCENT
    BOUND WITH MG  /    3.5 PERCENT
    BOUND WITH NA  /    0.2 PERCENT
```

SECTION 6

OPEN SYSTEMS

GEOCHEM can calculate the equilibrium speciation and set of solid phases in a soil solution that is free to exchange CO_2 and N_2 with the soil atmosphere. An exchange of O_2 with the soil atmosphere also can be treated indirectly by adjustment of the pE value, since

$$\log p_{O_2} = -83.1 + 4pH + 4pE \qquad (18)$$

where p_{O_2} is the partial pressure of O_2 in atmospheres (Stumm and Morgan, 1970, p. 309). If the soil atmosphere is in equilibrium with the terrestrial surface atmosphere, $p_{CO_2} = 10^{-3.5}$ atm. and $p_{N_2} = 10^{-0.1}$ atm. Otherwise, the partial pressures of CO_2 and N_2 may be adjusted in the input data to fit the soil conditions which prevail.

For convenience in computation, CO_2 and N_2 are manipulated in the same way as are solid phases in the program. CO_2 will be listed as "solid" H_2CO_3 and N_2 will be listed as "solid" $H_{12}(NO_3)_2$ in the outputs from the subroutines OUTCST, OUT1, and OUT138. There is no provision for O_2 as a "solid" in the program. In order to prescribe an equilibrium with a given partial pressure of this gas, Eq. (6.1) must be solved for the corresponding pE value (at a given pH value) and a redox computation must be performed as described in section 4.

In order to introduce $CO_2(g)$ as a component in the system, there is a need only to enter CO_3 as one of the ligands and to prepare Card No. 6 as follows:

Card No. 6. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of $-\log p_{CO_2}$ for the first set of concentration data.

6-10, etc.	Repeat the procedure for the second case, etc., up to 10. If "0" is entered at any point, the preceding value of $-\log p_{CO_2}$ is understood. For example, a 3.5 in columns 1-5 followed by "0" in columns 6-10, 11-15, and 16-20 means $-\log p_{CO_2} = 3.5$ for cases 1, 2, 3, and 4.

The value of p_{CO_2} and the pH value are sufficient to determine the carbonate equilibrium in any open soil solution, even when complexes form between CO_3^{2-}, H^+, and the metal cations in the system. Therefore, the value of $-\log CO_{3T}$ entered on the carbonate ligand card is redundant chemically. However, it is required computationally in order to avoid the situation where H_2CO_3 "dissolves" (i.e., $CO_2(g)$ disappears into the atmosphere) during the iterations. If this happens, it means that not enough total carbonate was put into the system to maintain an equilibrium with the imposed partial pressure of CO_2. Accordingly, it is important that the value of $-\log CO_{3T}$ entered be small enough to allow the speciation of carbonate to occur as well as equilibrium with the atmosphere. As a rule, $-\log CO_{3T} = 1.0$ should be sufficiently small, but the value chosen is arbitrary. If the concentration of carbonate imposed is in excess, the program will report that H_2CO_3 "precipitates", meaning that the excess CO_2 has escaped to the atmosphere. This does not affect the value of p_{CO_2} imposed because the atmosphere is a CO_2 reservoir and it does not alter the carbonate speciation because that depends only on pH and p_{CO_2}.

In some cases a soil solution is in equilibrium with CO_2 at a partial pressure that is greater than $10^{-3.5}$ atm. and the value of CO_{3T} can be determined rapidly enough after extraction of the solution that it represents an input concentration for the system that is chemically significant and not arbitrary. For this situation it is the value of p_{CO_2} that should be adjusted while that of CO_{3T} is maintained on the carbonate ligand card at the measured value. The most straightforward procedure is to run the analytical data as several cases in the calculation by GEOCHEM, with the only difference among the cases being in the value of $-\log p_{CO_2}$ on Card No. 6. Those values of $-\log p_{CO_2}$ that result in H_2CO_3 "dissolving" are too large for the system. The largest value of $-\log p_{CO_2}$ that results in H_2CO_3 "precipitating" is the one that equals the true-equilibrium value. This value usually can be determined by trial and error after running a few cases. The resulting speciation and solid phase composition calculated by GEOCHEM then represent equilibrium for the soil solution under the value of p_{CO_2} deduced.

If a soil solution is free to exchange N_2 with its surroundings, chemical effects can be expected only if redox equilibria are considered, since the aqueous species of nitrogen contain N in oxidation states different from zero. Therefore, in order to include an imposed N_2 partial pressure in an equilibrium calculation performed by GEOCHEM, the procedures described in section 4 must be followed. Card Nos. 7 and 10 must be included along with a ligand card for NO_3 and Card No. 8 must be prepared as follows:

Card No. 8. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of $-\log p_{N_2}$ for the first set of concentration data.
6-10, etc.	Repeat the procedure for the second case, etc., up to 10. If "0" is entered at any point, then the preceding value of $-\log p_{N_2}$ is understood.

The value of p_{N_2} will almost always be $10^{-0.1}$ atm. It is important once again to prevent the gas phase from escaping ($H_{12}(NO_3)_6$ "dissolves") during the calculation by imposing a small enough value of $-\log NO_{3T}$ in the nitrate ligand card. If there is some reason to believe that the value of NO_{3T} should be fixed during the computation, then $-\log p_{N_2}$ can be adjusted in trial-and-error runs, as described for CO_2.

SECTION 7

INTERACTION INTENSITIES AND CAPACITIES

In a complicated, multicomponent chemical system such as a soil solution, it is necessary to employ a computer program like GEOCHEM in order to account in detail for the many reactions that occur. For each set of concentration data that describes a given soil solution, the speciation of the components and the array of solid phases to be found at equilibrium are summarized in a detailed fashion by the percentage distribution tables printed as the output from the subroutine OUT138. Often it is desired to learn how the percentage distribution will shift in response to changes in pH, pE, CO_2 partial pressure, or the total concentrations of certain components of a soil solution. In this case, several runs of GEOCHEM can be made for the different imposed conditions and the output from OUT138 can be examined for trends.

An alternative to a case-by-case examination of percentage distribution figures is the computation of interaction intensities and capacities. These quantities are defined expressly for the purpose of elucidating the principal pathways of interaction in a multicomponent chemical system. The interaction capacity for a pair of components, X, Y, is defined by the expression:

$$\delta'_{X,Y} = \frac{\partial pX}{\partial TOTY} \tag{19}$$

where pX = -log [X], [X] is the molar free ionic concentration of component X, and TOTY is the total molar concentration of component Y. The partial derivative in Eq. (19) is carried out with all components but X and Y held at a fixed total concentration. The well known pH buffer capacity is a special case of an interaction capacity:

$$\beta_H = \frac{\partial TOTH}{\partial pH} = 1/\delta'_{H,H} \tag{21}$$

Except for H, the value of TOTY for any metal or ligand component in a soil solution will be a non-negative number. This fact makes it possible to define a dimensionless quantity called the interaction intensity of two components X and Y:

$$\delta_{X,Y} = \frac{\partial pX}{\partial pTOTY} \qquad (21)$$

where pTOTY is the negative common logarithm of the total concentration of component Y ($Y \neq H$) in the system. Clearly

$$\delta_{X,Y} = -2.303 TOTY \; \delta'_{X,Y} \qquad (22)$$

for any component $Y \neq H$.

The concepts of interaction intensities and capacities have been discussed at length with many examples by Morel et al. (1973, 1976). As a general rule, a large absolute value of $\delta_{X,Y}$ corresponds to a very great dependence of the free ionic concentration of X on the total concentration of Y in the system. If $\delta_{X,Y} > 0$ and large, the free ionic concentration of X increases greatly when the amount of Y in the system increases. If $\delta_{X,Y} < 0$ and its absolute value is large, the free ionic concentration of X drops significantly when the amount of Y increases. If $\delta_{X,Y} = 0$, the presence of Y in the system has little effect on the chemistry of X. By examining a table of interaction intensities for a given set or sets of analytical data, one can usually identify quite directly the major interaction webs among the components of a soil solution. Often most of the values of $\delta_{X,Y}$ will be very small and the principal set of components that determines the chemical fate of a chosen metal or ligand X can be established almost at a glance. Several examples of tables of $\delta_{X,Y}$ values are presented by Morel et al. (1973, 1976) and Ingle et al. (1978).

As an illustration of the application of interaction intensities, Fig. 2 shows a plot of the absolute value of $\delta_{Cd,Y}$ against pH for an aqueous solution containing the metals and ligands listed in Table 30. The data shown in Fig. 2 were adapted directly from Morel et al. (1973). For pH values below 6.2, where $CdCO_3(s)$ does not precipitate, the concentration of Cd^{2+} depends almost entirely on the total concentration of Cd in the system, with some considerably smaller dependence on the total concentrations of complexing ligands such as Cl^- and SO_4^{2-}. The dependence of $[Cd^{2+}]$ on Ca is not large and comes principally through the effect of Ca on sulfate and carbonate ligands. Above pH 6.2, $CdCO_3(s)$ precipitates in the system and $\delta_{Cd,CO_3} = -1$ until $CaCO_3(s)$ precipitates at pH 8.4. The values of $\delta_{Cd,Cd}$ and $\delta_{Cd,Cl}$ now decrease considerably and $\delta_{Cd,Ca}$ grows as the Ca present titrates the CO_3^{2-} which increases with the pH value.

TABLE 30. THE SYSTEM CONSIDERED IN RELATION TO FIGURE 2

Metal	pC	Metal	pC	Ligand	pC
Ca	3.00	Zn	7.00	CO_3	3.00
Mg	3.50	Ni	6.50	SO_4	4.50
Na	3.50	Hg	9.00	Cl	3.50
Fe	5.00	Pb	7.00	F	5.50
Mn	5.50	Co	7.50	NH_3	5.50
Cu	6.00	Ag	9.00	PO_4	5.00
Ba	7.00	Al	5.00	SiO_3	4.00
Cd	6.00	H	—	OH	—

The interaction capacities can be used to compute approximate changes in pX following small changes in a Y component. As an example, the use of interaction capacities to compute pH has been illustrated by Morel et al. (1976).

Interaction intensities and capacities are computed by GEOCHEM if the appropriate entries are made on Card No. 1. In card columns 31-33, a "0" entered means "no interaction intensities or capacities are computed", a "1" entered means "compute and print interaction capacities", and a "2" entered means "compute and print interaction intensities", and a "3" entered means "compute and print both interaction intensities and capacities. The subroutine OUTJAC computes and prints these quantities. Note that $\acute{X}_{,H}$ is always printed instead of $_{X,H}$, even if a "2" is entered. OUTJAC prints components X vertically and components Y horizontally in the table of $\acute{X}_{,Y}$ or $_{X,Y}$ values. Typical output of $\acute{X}_{,Y}$ and $_{X,Y}$ values are shown in Table 31 for the system in Table 30 at a pH value of 6.0.

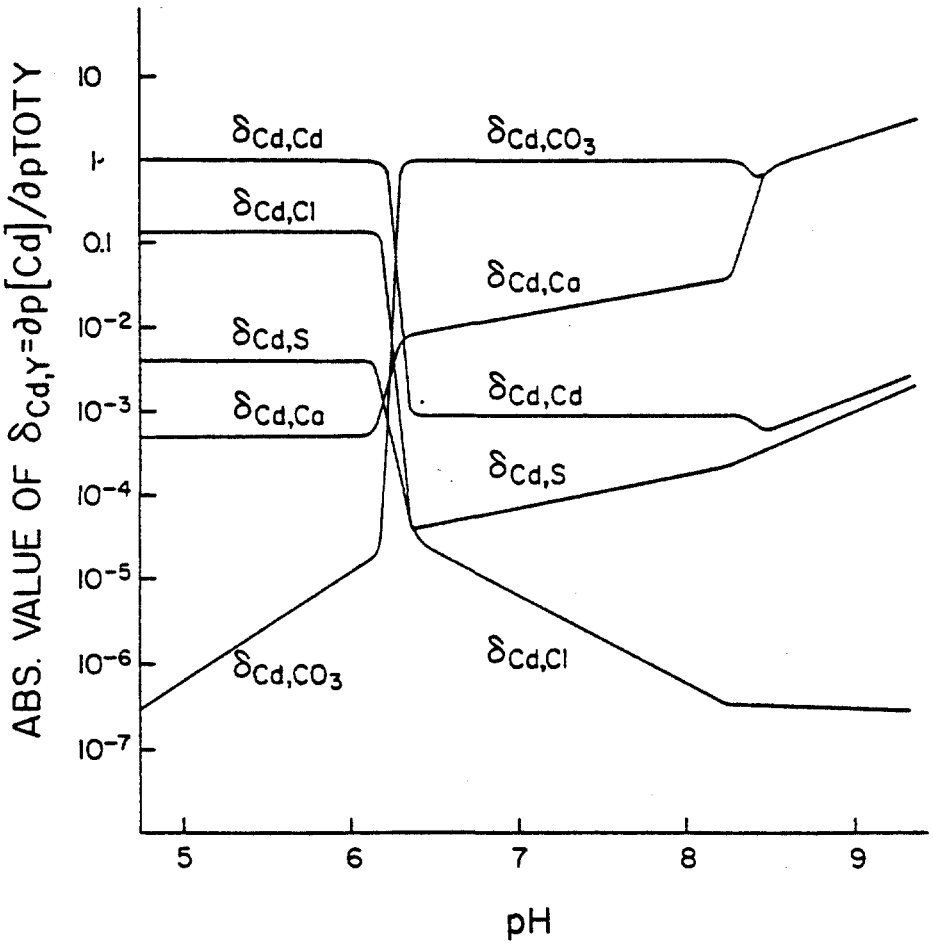


Figure 2. Graph of the absolute value of $\delta_{Cd,Y}$ versus pH for the system described in Table 30 (after Morel et al. (1973).

TABLE 31. OUTPUT FROM THE SUBROUTINE OUTJAC FOR THE SYSTEM DESCRIBED IN TABLE 30

INTERACTION CAPACITIES:

	CA	MG	NA	FE3	MN	CU2+	BA	CD	ZN	NI	PB
CA	-4.34E 02	-1.43E-01	-1.43E-02	-1.38E 01	-2.92E-01	-3.77E 00	-1.49E-01	-2.21E-01	-7.00E-01	-1.10E 00	-5.92E 00	-2.00E 00
MG	-1.43E-01	-1.37E 03	-1.17E-02	-1.20E 01	-2.58E-01	-3.23E 00	-1.19E-01	-1.82E-01	-6.52E-01	-1.00E 00	-4.70E 00	-2.49E 00
NA	-1.43E-02	-1.17E-02	-1.37E 03	-1.80E 00	-2.70E-02	-5.02E-01	-1.19E-02	-2.46E-02	-9.18E-02	-1.51E-01	-8.82E-01	-5.70E-01
FE3	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.08E 02	-3.53E 03	5.44E-03	-4.04E 01	-5.53E 02	-1.01E 03	-5.38E 03	-2.68E 03
MN	-2.92E-01	-2.58E-01	-2.70E-02	-1.08E 02	-1.37E 05	-2.93E 01	-1.40E-01	-3.01E-01	-4.01E 00	-6.47E 00	-3.23E 01	-2.10E 01
CU2+	-3.77E 00	-3.20E 00	-5.02E-01	-3.53E 03	-2.93E 01	-4.35E 05	-3.29E-02	-1.12E 01	-1.53E 02	-2.79E 02	-1.03E 03	-7.10E 02
BA	-1.49E-01	-1.19E-01	-1.19E-02	5.43E-03	-1.40E-01	-3.29E-02	-4.34E 06	-1.50E-01	-1.04E-01	-1.15E-01	-5.02E-01	-1.29E-01
CD	-2.21E-01	-1.82E-01	-2.46E-02	-4.04E 01	-5.01E-01	-1.12E 01	-1.50E-01	-4.34E 03	-1.92E 00	-3.20E 00	-4.75E 01	-6.42E 00
ZN	-7.00E-01	-6.52E-01	-9.18E-02	-5.53E 02	-4.01E 00	-1.53E 02	-1.04E-01	-1.92E 00	-4.34E 06	-4.37E 01	-1.04E 02	-1.13E 02
NI	-1.18E 00	-1.00E 00	-1.51E-01	-1.01E 03	-8.47E 00	-2.79E 02	-1.15E-01	-3.20E 00	-4.37E 01	-1.37E 06	-2.98E 02	-2.04E 02
HG	-4.52E 00	-3.94E 00	-8.32E-01	-5.38E 03	-3.24E 01	-1.04E 03	-3.65E-01	-3.03E 01	-1.04E 02	-2.98E 02	-4.54E 06	-7.98E 02
PB	-2.88E 00	-2.45E 00	-3.70E-01	-2.68E 03	-2.16E 01	-7.18E 02	-1.29E-01	-8.42E 00	-1.13E 02	-2.04E 02	-7.99E 02	-4.34E 06
CO3+	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.08E 02	-3.53E 03	5.44E-03	-4.04E 01	-5.53E 02	-1.01E 03	-5.38E 03	-2.68E 03
AG	-3.53E-01	-2.81E-01	-6.38E-02	-5.18E-02	-7.94E-02	-5.15E-02	-6.11E-02	-8.43E 00	-6.20E-02	-3.83E-02	-4.00E 02	-1.51E 00
AL	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.08E 02	-3.53E 03	5.39E-03	-4.04E 01	-5.53E 02	-1.01E 03	-5.38E 03	-2.68E 03
CO3-	5.05E 00	7.73E 00	1.20E 03	1.03E 04	7.10E 01	2.35E 03	-2.47E-03	2.68E 01	3.68E 02	6.69E 02	3.04E 03	1.75E 03
SO4	4.50E 01	5.58E 01	3.60E 00	2.33E 00	4.40E 01	1.05E 01	4.51E 01	4.37E 01	4.95E 01	3.48E 01	8.75E-01	5.93E 01
CL	1.30E 00	1.03E 00	3.13E-01	7.73E-02	2.66E-01	1.65E-01	2.72E-01	3.17E 01	1.94E-01	1.13E-01	1.53E 03	5.64E 00
F	3.22E 00	2.01E 01	1.28E-02	4.92E 01	3.29E-01	1.07E 01	6.40E-01	4.00E 00	7.04E 00	5.82E 00	1.46E 01	1.00E 01
NH3	4.59E 00	3.99E 00	6.00E-01	6.05E 03	3.60E 01	1.22E 03	-1.81E-03	1.36E 01	1.84E 02	3.30E 02	1.79E 03	6.92E 02
PO4	2.93E 01	3.48E 01	1.05E 00	1.15E 04	1.45E 02	2.25E 03	1.99E 00	3.82E 01	3.91E 02	6.56E 02	3.40E 03	1.71E 03
SIO3	9.18E 00	7.99E 00	1.20E 03	1.21E 04	7.20E 01	2.35E 03	-3.57E-03	2.70E 01	3.69E 02	6.72E 02	3.59E 03	1.70E 03
H	-4.59E 00	-4.00E 00	-6.01E-01	-6.06E 03	-3.60E 01	-1.18E 03	1.81E-03	-1.35E 01	-1.84E 02	-3.30E 02	-1.79E 03	-8.92E 02

TABLE 31. (Continued)

	CO3+	AG	AL	CO3-	SO4	CL	F	NH3	PO4	SIO3	H
CA	-1.38E 01	-3.53E-01	-1.38E 01	9.05E 00	4.50E 01	1.30E 00	3.22E 00	4.59E 00	2.93E 01	9.16E 00	-4.59E 00
MG	-1.20E 01	-2.81E-01	-1.20E 01	7.76E 00	3.58E 01	1.03E 00	2.01E 01	3.99E 00	3.48E 01	7.99E 00	-4.00E 00
NA	-1.80E 00	-8.38E-02	-1.80E 00	1.20E 00	3.00E 00	3.13E-01	1.28E-02	6.00E-01	1.85E 00	1.20E 00	-6.01E-01
FE3	-1.82E 04	-5.43E-02	-1.82E 04	1.03E 04	2.33E 00	7.70E-02	4.92E 01	6.05E 03	1.15E 04	1.21E 04	-6.06E 03
MN	-1.08E 02	-7.95E-02	-1.08E 02	7.10E 01	4.40E 01	2.65E-01	3.29E-01	3.60E 02	1.45E 02	7.20E 01	-3.60E 01
CU2+	-3.53E 03	-5.09E-02	-3.53E 03	2.35E 03	1.05E 01	1.62E-01	1.07E 01	1.22E 03	2.25E 03	2.35E 03	-1.18E 03
BA	5.43E-03	-8.11E-02	5.37E-03	-2.47E-03	4.51E 01	2.72E-01	6.40E-01	-1.80E-03	1.99E 00	-3.50E-03	1.81E-03
CD	-4.04E 01	-8.43E 00	-4.04E 01	2.68E 01	4.37E 01	3.17E 01	4.00E 00	1.36E 01	5.82E 01	2.70E 01	-1.35E 01
ZN	-5.53E 02	-6.20E-02	-5.53E 02	3.68E 02	4.95E 01	1.94E-01	7.04E 00	1.84E 02	3.91E 02	3.69E 02	-1.84E 02
NI	-1.01E 03	-3.85E-02	-1.01E 03	6.69E 02	3.48E 01	1.13E-01	5.82E 00	3.36E 02	6.56E 02	6.72E 02	-3.36E 02
HG	-5.38E 03	-1.31E 02	-5.38E 03	3.04E 03	7.50E-01	1.49E 03	1.46E 01	1.79E 03	3.40E 03	3.59E 03	-1.79E 03
PB	-2.68E 03	-1.51E 00	-2.68E 03	1.75E 03	3.93E 01	5.64E 00	1.00E 01	8.92E 02	1.71E 03	1.78E 03	-8.92E 02
CO3+	-1.82E 04	-5.43E-02	-1.82E 04	1.03E 04	2.33E 00	7.70E-02	4.92E 01	6.05E 03	1.15E 04	1.21E 04	-6.06E 03
AG	-5.18E-02	-4.34E 06	-5.18E-02	3.07E-02	2.70E 00	3.65E 02	6.91E-03	5.14E-01	5.54E-02	3.45E-02	-1.73E-02
AL	-1.82E 04	-5.57E-02	-2.30E 04	1.03E 04	2.33E 00	7.67E-02	6.08E 01	6.05E 03	1.15E 04	1.09E 04	-6.06E 03
CO3-	1.03E 04	3.31E-02	1.03E 04	-6.22E 03	-1.49E 00	-4.94E-02	-2.70E 01	-3.42E 03	-6.47E 03	-6.84E 03	3.42E 03
SO4	2.33E 00	2.70E 00	2.33E 00	-1.49E 00	-1.37E 04	-1.65E-01	-8.59E-01	-7.79E-01	-4.35E 00	-1.50E 00	7.70E-01
CL	7.73E-02	3.65E 02	7.73E-02	-4.90E-02	-1.65E-01	-1.37E 03	-2.51E-02	-2.58E-02	-1.32E-01	-5.15E-02	2.58E-02
F	4.92E 01	6.92E-03	6.08E 01	-2.78E 01	-8.59E-01	-2.51E-02	-1.37E 03	-1.64E 01	-3.16E 01	-4.44E 01	1.64E 01
NH3	6.05E 03	5.15E-01	6.05E 03	-3.42E 03	-7.79E-01	-2.57E-02	-1.64E 01	-1.39E 03	-3.82E 03	-4.03E 03	2.02E 03
PO4	1.15E 04	5.79E-02	1.15E 04	-6.47E 03	-4.35E 00	-1.32E-01	-3.16E 01	-3.82E 03	-5.07E 04	-7.65E 03	3.82E 03
SIO3	1.21E 04	3.76E-02	1.69E 04	-6.84E 03	-1.56E 00	-5.10E-02	-4.44E 01	-4.03E 03	-7.65E 03	-1.29E 04	4.04E 03
H	-6.06E 03	-1.81E-02	-6.06E 03	3.42E 03	7.70E-01	2.57E-02	1.64E 01	2.02E 03	3.82E 03	4.04E 03	-2.02E 03

TABLE 31. (Continued)

INTERACTION INTENSITIES:

	CA	MG	NA	FE3	MN	CU2+	BA	CD	ZN	NI	HG	PB
CA	1.00E 00	1.04E-04	1.04E-05	3.17E-04	2.13E-06	8.63E-06	3.43E-06	5.10E-07	1.76E-07	8.62E-07	1.27E-08	6.63E-07
MG	3.30E-04	1.00E 00	8.49E-06	2.70E-04	1.88E-06	7.38E-06	2.74E-08	4.19E-07	1.50E-07	7.32E-07	1.08E-08	5.64E-07
NA	3.30E-05	8.49E-06	1.00E 00	4.15E-05	2.02E-07	1.16E-06	2.75E-09	5.05E-08	2.11E-08	1.10E-07	2.03E-09	8.70E-08
FE3	3.17E-02	8.73E-03	1.31E-03	4.19E-01	7.87E-04	8.13E-03	-1.25E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.17E-04
MN	8.73E-04	1.88E-04	2.02E-05	2.49E-03	1.00E 00	8.75E-05	3.41E-08	1.15E-06	1.11E-06	8.17E-06	7.43E-08	4.99E-06
CU2+	8.08E-03	2.33E-03	3.66E-04	8.13E-02	2.14E-04	1.00E 00	7.58E-09	2.57E-05	5.53E-05	2.03E-04	2.41E-06	1.65E-04
BA	3.43E-04	8.67E-05	8.68E-06	-1.25E-07	1.08E-06	7.58E-08	1.00E 00	3.46E-07	3.78E-08	8.36E-08	6.95E-10	2.58E-08
CD	5.10E-04	1.33E-04	1.79E-05	9.31E-04	3.65E-06	2.57E-05	3.46E-08	1.00E 00	4.41E-07	2.39E-06	1.09E-07	1.54E-06
ZN	1.76E-03	4.74E-04	6.09E-05	1.27E-02	3.51E-05	3.53E-04	3.78E-08	4.41E-06	1.00E 00	5.19E-05	3.77E-07	2.59E-05
NI	2.73E-03	7.32E-04	1.10E-04	2.32E-02	6.17E-05	6.41E-04	2.64E-08	7.56E-06	1.01E-05	1.00E 00	6.67E-07	4.71E-05
HG	1.04E-02	2.87E-03	5.84E-04	1.24E-01	2.36E-04	2.41E-03	8.40E-08	8.98E-05	3.77E-05	2.17E-04	1.00E 00	1.84E-04
PB	6.63E-03	1.78E-03	2.75E-04	6.17E-02	1.58E-04	1.65E-03	2.98E-08	1.94E-05	2.59E-05	1.49E-04	1.64E-06	1.00E 00
CO3+	3.17E-02	8.73E-03	1.31E-03	4.19E-01	7.87E-04	8.13E-03	-1.25E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.17E-04
AG	8.13E-04	2.04E-04	8.10E-05	1.19E-06	5.79E-07	1.18E-07	1.87E-08	1.94E-05	1.43E-06	2.79E-08	9.35E-07	3.48E-07
AL	3.17E-02	8.73E-03	1.31E-03	4.19E-01	7.87E-04	8.13E-03	-1.24E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.16E-04
CO3-	-2.08E-02	-5.67E-03	-8.73E-04	-2.36E-01	-5.17E-04	-5.41E-03	5.69E-10	-6.17E-05	-8.47E-05	-4.87E-04	-6.99E-06	-4.03E-04
SO4	-1.04E-01	-2.60E-02	-2.62E-03	-5.38E-05	-3.21E-04	-2.42E-05	-1.04E-05	-1.01E-04	-1.14E-05	-2.54E-05	-2.01E-09	-9.06E-06
CL	-2.99E-03	-7.51E-04	-2.26E-04	-1.78E-06	-1.94E-06	-3.75E-07	-6.27E-08	-7.30E-05	-4.47E-08	-6.20E-08	-3.52E-06	-1.30E-06
F	-7.41E-03	-1.47E-02	-9.33E-06	-1.13E-03	-2.40E-06	-2.46E-05	-1.47E-07	-9.22E-06	-1.62E-06	-4.24E-06	-3.36E-08	-2.31E-06
NH3	-1.06E-02	-2.91E-03	-4.37E-04	-1.39E-01	-2.62E-04	-2.81E-03	4.17E-10	-3.13E-05	-4.24E-05	-2.45E-04	-4.13E-06	-2.05E-04
PO4	-6.75E-02	-2.54E-02	-1.35E-03	-2.64E-01	-1.06E-03	-5.18E-03	-4.59E-07	-8.80E-05	-9.01E-05	-4.79E-04	-7.82E-06	-3.54E-04
SIO3	-2.11E-02	-5.82E-03	-8.75E-04	-2.79E-01	-5.24E-04	-5.42E-03	8.23E-10	-6.21E-05	-8.49E-05	-4.89E-04	-8.26E-06	-4.11E-04
H	1.06E-02	2.91E-03	4.38E-04	1.40E-01	2.62E-04	2.71E-03	-4.18E-10	3.10E-05	4.25E-05	2.45E-04	4.13E-06	2.06E-04

TABLE 31. (Continued)

	CO3+	AG	AL	CO3-	SO4	CL	F	NH3	PO4	SIO3	H
CA	1.00E-04	8.13E-10	3.17E-04	-2.08E-02	-3.27E-03	-9.44E-04	-2.34E-05	-3.34E-05	-6.75E-04	-2.11E-03	-4.59E 00
MG	8.73E-07	6.47E-10	2.76E-04	-1.79E-02	-2.60E-03	-7.51E-04	-1.47E-04	-2.91E-05	-8.02E-04	-1.84E-03	-4.00E 00
NA	1.31E-07	1.93E-10	4.15E-05	-2.76E-03	-2.62E-04	-2.28E-04	-9.33E-08	-4.37E-06	-4.26E-05	-2.77E-04	-6.01E-01
FE3	1.32E-03	1.25E-10	4.19E-01	-2.36E 01	-1.70E-04	-5.61E-05	-3.58E-04	-4.41E-02	-2.64E-01	-2.79E 00	-6.06E 03
MN	7.87E-06	1.83E-10	2.49E-03	-1.64E-01	-3.21E-03	-1.94E-04	-2.40E-06	-2.62E-04	-3.34E-03	-1.66E-02	-3.60E 01
CU2+	2.57E-04	1.17E-10	8.13E-02	-5.41E 00	-7.65E-04	-1.18E-04	-7.70E-05	-8.90E-03	-5.18E-02	-5.42E-01	-1.18E 03
BA	-3.96E-10	1.87E-10	-1.24E-07	5.66E-06	-3.29E-03	-1.98E-04	-4.66E-06	1.31E-08	-4.59E-05	8.20E-07	1.81E-03
CD	2.95E-06	1.94E-08	9.31E-04	-6.17E-02	-3.18E-03	-2.31E-02	-2.91E-05	-9.90E-05	-6.80E-04	-6.21E-03	-1.35E 01
ZN	4.03E-05	1.43E-10	1.27E-02	-8.47E-01	-3.60E-03	-1.41E-04	-5.12E-05	-1.34E-03	-9.01E-03	-8.49E-02	-1.84E 02
NI	7.34E-05	8.87E-11	2.32E-02	-1.54E 00	-2.54E-03	-8.20E-05	-4.24E-05	-2.45E-03	-1.52E-02	-1.55E-01	-3.36E 02
HG	3.92E-04	3.01E-07	1.24E-01	-6.99E 00	-5.51E-05	-1.09E 00	-1.06E-04	-1.30E-02	-7.82E-02	-8.26E-01	-1.79E 03
PB	1.95E-04	3.48E-09	6.16E-02	-4.03E 00	-2.86E-03	-4.11E-03	-7.29E-05	-6.49E-03	-3.94E-02	-4.11E-01	-8.92E 02
CO3+	1.32E-03	1.25E-10	4.19E-01	-2.36E 01	-1.70E-04	-5.61E-05	-3.58E-04	-4.41E-02	-2.64E-01	-2.79E 00	-6.06E 03
AG	3.77E-09	1.00E 00	1.19E-06	-7.07E-05	-1.97E-04	-2.65E-01	-5.03E-08	-3.74E-06	-1.28E-06	-7.96E-06	-1.73E-02
AL	1.32E-03	1.20E-10	5.29E-01	-2.36E 01	-1.70E-04	-5.58E-05	-4.42E-04	-4.41E-02	-2.64E-01	-3.90E 00	-6.06E 03
CO3-	-7.47E-04	-7.63E-11	-2.36E-01	1.43E 01	1.09E-04	3.60E-05	2.02E-04	2.49E-02	1.49E-01	1.57E 00	3.42E 03
SO4	-1.70E-07	-6.23E-09	-5.36E-05	3.44E-03	1.00E 00	1.20E-04	6.26E-06	5.67E-06	1.00E-04	3.58E-04	7.78E-01
CL	-5.63E-09	-6.40E-07	-1.78E-06	1.13E-04	1.20E-05	1.00E 00	1.83E-07	1.88E-07	3.04E-06	1.19E-05	2.58E-02
F	-3.58E-06	-1.59E-11	-1.40E-03	8.40E-02	8.26E-05	1.83E-05	9.98E-01	1.19E-04	7.28E-04	1.02E-02	1.64E 01
NH3	-4.41E-04	-1.19E-09	-1.39E-01	7.87E 00	5.67E-05	1.86E-05	1.19E-04	1.01E 00	8.80E-02	9.29E-01	2.02E 03
PO4	-8.36E-04	-1.33E-10	-2.64E-01	1.49E 01	3.17E-04	9.59E-05	2.30E-04	2.78E-02	1.17E 00	1.76E 00	3.82E 03
SIO3	-8.82E-04	-8.67E-11	-3.90E-01	1.57E 01	1.13E-04	3.71E-05	3.23E-04	2.94E-02	1.76E-01	2.97E 00	4.04E 03
H	4.41E-04	4.17E-11	1.40E-01	-7.87E 00	-5.67E-05	-1.87E-05	-1.19E-04	-1.47E-02	-8.81E-02	-9.30E-01	-2.02E 03

SECTION 8

THE THERMODYNAMIC DATA IN GEOCHEM

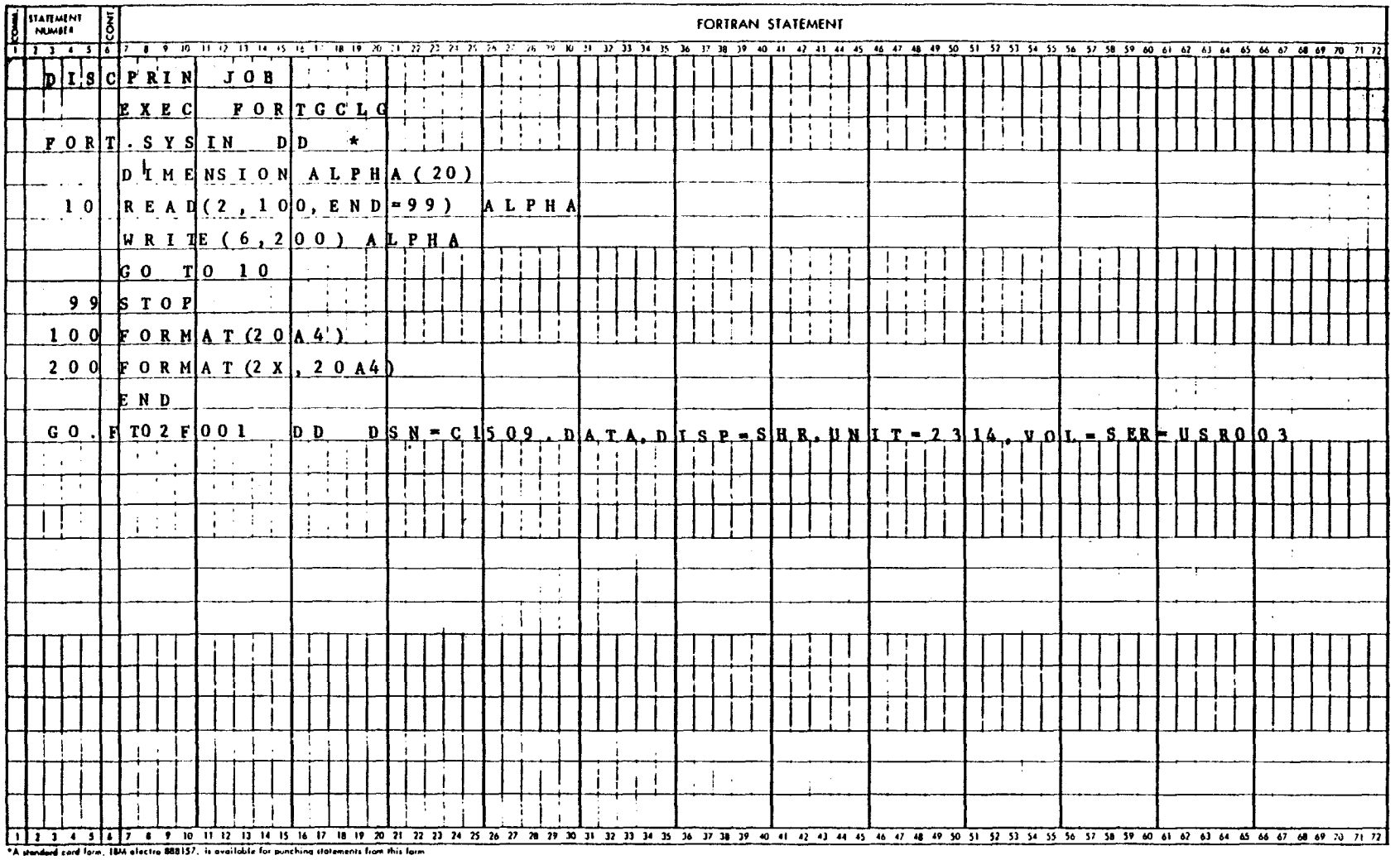
THE THERMODYNAMIC DATA FILE

The thermodynamic data stored in GEOCHEM are thermodynamic equilibrium constants and stoichiometric coefficients for soluble complexes, solids, and redox couples. These data have been compiled with a great deal of care, but they should be reviewed frequently and compared to new data on reactions of interest that appear in the chemical, geochemical, and soil chemical literature. Useful critical compilations, such as those by Martell and Smith (1976-77), Baes and Mesmer (1976), Robie et al. (1978), and Sadiq and Lindsay (1979) should be consulted often. It is very important to keep in mind that the calculational results produced by GEOCHEM can never be any better than the thermodynamic data it contains. A brief discussion of the methodologies involved in selecting thermodynamic equilibrium constants has been given by Sposito and Mattigod (1977, Appendix).

At present GEOCHEM can store up to six thermodynamic stability constants for soluble complexes and up to three thermodynamic formation constants for solids for each possible metal-ligand combination. These maximal numbers have not been reached for many of the combinations as yet, so much more data can be added. To examine the data file in GEOCHEM, one should have it printed out; control cards to print data stored on disc in an IBM 370/155 system are shown in Figure 3. These cards require modification for other computing systems. If the data file is to be modified, it should be punched onto cards using the appropriate control cards. The data deck produced in this way is described in the next section.

ADDING NEW THERMODYNAMIC DATA

Modifications of the existing thermodynamic equilibrium constants in GEOCHEM or the addition of equilibrium constants for metal-ligand combinations not already in the program can be accomplished by preparing a new thermodynamic data deck and transferring it to the disc storage location accessed by GEOCHEM when it performs a calculation. The control cards that transfer the data deck should be developed in consultation with the user's computer center. The data deck that comes after these control cards has the following structure:



*A standard card form, IBM electro 888157, is available for punching statements from this form

Figure 3. Control cards for printing the thermodynamic data file in GEOCHEM.

TABLE 32. THE THERMODYNAMIC DATA FILE IN GEOCHEM

Card No.	Format	Card Col.	Type of Information Entered
1	2I3	1-3	Total number of metals in the data file, including H^+
		4-6	Total number of ligands in the data file, including OH^-
2	I2,I3, F7.2	1-2	Code number of metal
		3-5	Valence of metal
		6-12	Ionic radius of metal, in $\mathring{A}$
3	I2,I3, F7.2	1-2	Code number of ligand
		3-5	Valence of ligand, including sign
		6-12	Ionic radius of ligand, in $\mathring{A}$
4	I5,F5.2, F5.1	1-5	Number of metal-ligand combinations considered by the program
		6-10	Value of $-\log K_w$ (enter "14.00")
		11-15	Value of -10 log K for the reaction: $2H^+ + CO_3^{2-} = CO_2(g) + H_2O$ (enter "182.0")
5	2I2, 9(I4, 2I1, I2)	1-2	Code number of metal
		3-4	Code number of ligand combined with metal
		5-8	Value of 10 log K for solid No. 1
		9	Stoichiometric coefficient of metal in solid
		10	Stoichiometric coefficient of ligand in solid
		11-12	Stoichiometric coefficient of H or OH in solid (negative for OH, zero if no H or OH present)
		13-16	Value of 10 log K for solid No. 2
		17, 18, 19-20	Same as for columns 9, 10, 11-12
		21-24	Same as for columns 5-8,
		25, 26, 27-28	9, 10, 11-12
		29-32	Value of 10 log K for complex No. 1
	—	33	Stoichiometric coefficient of metal in complex
		34	Stoichiometric coefficient of ligand in complex

Continued

TABLE 32. (Continued)

Card No.	Format	Card Col.	Type of Information Entered
		35-36	Stoichiometric coefficient of H or OH in complex (< 0 for OH, "0" if no H or OH present)
		37-40	This sequence is repeated for each
		41	complex formed by the metal-
		42	ligand combination, up to 6 in
		43-44	total
6	I5	1-5	Number of redox reactions considered by the program, up to 30 (24 presently in GEOCHEM)
7	9I5, A8	1-5	Redox reaction No. from Table 2
		6-10	Code number of reactant metal or ligand
		11-15	Code number of product metal or ligand, or of second reactant metal or ligand if a complex or solid is formed.
		16-20	+10 if two ligands involved, +9 to +1 if a metal-ligand complex is involved, -1 to -9 if a solid is involved, -10 if two metals involved (Table 2, "Reaction Type")
		21-25	Value of NE (Tables 2 and 18)
		26-30	Value of NH (Tables 2 and 18)
		31-35	Value of 10 log K (Table 2)
		36-40	Stoichiometric coefficient of species entered in col. 6-10 (Enter "0" if $\pm$10 was entered in col. 16-20 or if the species is H^+. See column CM in Table 2)
		41-45	Stoichiometric coefficient of species entered in col. 11-15 (Enter "0" if $\pm$10 was entered in col. 16-20 or if the species is OH^-. See column CL in Table 2)
		46-53	Alphanumeric name of reaction (Table 2)
8	I4	1-4	Number of mixed solids considered (presently 14)

Continued

TABLE 32. (Continued)

Card No.	Format	Card Col.	Type of Information Entered
9	11I4, I6, 2I3, A8	1-4	Code number of mixed solid (Table 1)
		5-8	Reaction code: "0" if solid contains up to 2 metals and 2 ligands besides H or OH; "1" if solid contains up to 4 metals besides Al^{3+} and $SiO_2(OH)_2^{2-}$
		9-12	Code number of first metal
		13-16	Code number of second metal (Enter 50 if no second metal)
		17-20	Code number of third metal or first ligand, or "50"
		21-24	Code number of fourth metal or "50", or second ligand or "99"
		25-28	Stoichiometric coefficients of the species entered in col. 9-12, 13-16, 17-20, and 21-24. Enter "0" if species is not present in the solid
		29-32	
		33-36	
		37-40	
		41-44	Number of H or OH in the solid (negative for OH). Do not count OH in $SiO_2(OH)_2^{2-}$
		45-50	Value of 10 log K, where K = equilibrium constant for the formation of the solid
		51-53	Number of Al^{3+} in solid
		54-56	Number of $SiO_2(OH)_2^{2-}$ in solid
		57-64	Alphanumeric name of the solid (Table 1.)

According to the list in Section 1, there are 36 metals and 69 ligands considered by the program. There also are 14 metal "slots" and 25 ligand "slots" available for new components. If new metals and ligands are being added, they should be accounted for in Card No. 1. The metal code numbers available are 36 to 49; the available ligand code numbers are 69 to 89. The code symbols for the metals are M36, M37, etc., and those for the ligands are L65, L66, etc.

Card No. 2 is repeated for every metal considered by the program. The ordering of the metal cards must be the same as in the list in Section 1.

Card No. 3 is repeated for every ligand considered by the program, in the proper order. New components are described in Card Nos. 2 and 3 in the same way as existing components. Their cards are placed last.

At present GEOCHEM considers 1034 metal-ligand combinations. The data on Card No. 4 may be altered if new complexes and solids are to be added or if better values of K_w and K become available.

The thermodynamic equilibrium constant for a solid is defined in section 3 and that for a complex is defined in section 2. In GEOCHEM, K for a solid equals the inverse of the solubility product constant and K for a complex equals the stability constant. Card No. 5 is repeated for every metal-ligand combination considered by the program, except HOH.

Card No. 7 is repeated for each redox reaction considered by the program. The last reaction entered <u>must</u> be $2\ NO_3^- + 12\ H^+ = N_2(g) + 6\ H_2O - 10\ e$.

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APPENDIX

Error Messages Generated by GEOCHEM

There are four error messages that are generated by the program when the data to be analyzed have not been specified properly. A listing of these error messages and the steps to take when they occur follow.

(1) BE CAREFUL NO CONVERGENCE.

This message will be generated whenever 500 iterations have been exceeded as the program attempts to solve the set of mole balance equations for the data under consideration. There are two principal causes for lack of convergence:

(a) If a large set of solid phases is precipitated during the computation, or simply for very large computations, the system may be converging although more iterations are required. In this case the remainders shown in the output from OUT1 will be smaller than the total concentrations used as the input data. To correct, run the computation again using the free concentrations shown in OUT1 as the guesses and imposing the precipitated solids listed there and no others. Alternatively, the number of iterations can be increased by inserting the following card immediately before Card No. 1. (See Card 0, section 1).

ITMAX Card. Format I3, 5X, E14.8.

Card Columns	Type of Information
1-3	Enter the maximum number of iterations permitted.
4-8	Blank
9-22	Enter the convergence criterion, i.e., the maximum value of EPS, where EPS = |calculated total conc. - input total conc.| ÷ input total conc.

(b) If the system has diverged, this can be ascertained by inspecting the values of the remainders in the table of free and total concentrations for the specific case. The remainder, R, is the difference between the computed and imposed analytical concentrations. If |R|/TOTX < EPS, specified on the ITMAX Card, the system is considered to be

converged. Thus, by comparing the remainders and total concentrations, the problem areas of the computation may be identified. Further information can be obtained from this listing of complex concentrations produced by OUT17. By hand computation on the problem subsystem, better input guesses of the free concentrations can be obtained. To correct, run again with better guesses of the free ionic concentrations and/or a different value of EPS.

There are two general situations in which convergence problems may be expected:

(1) If both a metal M and a ligand L are nearly all bound in a strong complex C (i.e., $^{C}K = [C]/[M][L]$ is very large) and the total concentration of the metal is approximately the same as the total concentration of the ligand. For example, $^{C}K = 10^{20}$, $[C] \simeq 10^{-2}$ M $\simeq$ total concentration of metal = total concentration of ligand, then $[M] = [L] = 10^{-11}$ M. But the mass-action equation is also satisfied within the precision of the program when $[M] = 10^{-13}$ M and $[L] = 10^{-9}$ M.

(2) If a solid is precipitated in very small amounts. For example, suppose that the total concentration of $Ca^{2+} = 10^{-1}$ M, the total concentration of $PO_4^{3-} = 10^{-8}$ M, and solid $Ca_5(PO_4)_3OH$ is present. Very small changes in the concentration of either Ca^{2+} or PO_4^{3-} can give very different solubility results because of the large stoichiometric coefficients in this solid.

(2) ERROR RETURN FROM GAUSSL DIAGONAL TERM REDUCED TO ZERO.

GAUSSL is the name of a Gaussian elimination subroutine which solves the system of nonliner mole balance equations. This error message will be generated if one of the diagonal elements of the computational matrix becomes equal to zero. It is not likely that this will happen if the input data have been specified properly. To correct, check the input concentration data for errors.

(3) REPEATED PRECIPITATION DISSOLUTION.

Under some circumstances the program will precipitate a solid phase and then dissolve it, repeatedly. It is likely, when this occurs, that another solid with the same metal-ligand combination should be precipitated instead. To correct, restart the computation with the suspected correct solid imposed.

(4) GIBBS PHASE RULE VIOLATED IN SUBSYSTEM.

This error message will be generated when a solid set is imposed which is inconsistent with Gibbs Phase Rule. As discussed in section 3.2, the program requires two degrees of freedom (T, P) in order to

choose the equilibrium constants. Generally the error occurs when too many solids are imposed in the initial solids set (this is the more likely situation), or the set, suspected to be correct, is not generated correctly by the program as a result of the order of precipitation. To correct, restart the computation with a set of imposed solids consistent with the phase rule.

The fact that, during a multi-case computation, the preceding case is used as a guess for the next case may also cause phase rule problems. When solids are precipitated in a preceding case, those solids are imposed on the next case and, if pE, pH or some other parameter is radically different between the two cases, those solids probably should not be imposed.

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GEOCHEM USER NOTES
Number 1

The GEOCHEM User Notes will be issued from time to time to bring users of the program up to date on new debugging developments, new subroutines, and modifications in the user's manual, either the BLUE or the WHITE version.

1. Manual Errors. Table 2.2 in the BLUE manual and Figure 1 in the WHITE manual show an incorrect format for data card No. 0 in the program. The correct format is given on page 19 of the BLUE manual and page 20 of the WHITE manual. It is: I3, 5X, E 14.8. Failure to follow this format will likely produce nonsensical output from the program (e.g., sum of metal species equal to more than 100%, etc.).

Page numbers 6, 33, and 34 are missing from the WHITE manual. No pages are missing. These page numbers were inadvertently not used when the manual was retyped.

2. Program Bugs.

(a) Subroutine INMIX. Card 28INMX40 in this subroutine presently reads: DO 500 K = 1, NMIX. This loop is executable, but it uses the index K both as a dummy loop index and, later, as a variable read in from the data file (in card 281NMX41). This double use of the same symbol will prevent FORTRAN Q compilers from compiling the program. The problem can be solved by changing card 28INMIX40 to read: DO 500 I = 1, NMIX.

(b) Subroutine TOTCC. As presently written, this subroutine will not respond properly to a value of 0 entered for -log total concentration of either a metal or a ligand in the first case. On page 14 of the BLUE manual and on page 14 of the WHITE manual, it states: "If the first case is 0, program assumes 1 M total concentration." As written, the program will in fact set the concentration equal to 0 M if 0 is entered for -log total concentration of metal or ligand in the first case. This will result in an overflow diagnostic.

To remedy the problem, the following cards should be inserted in TOTCC:

(i) After card 16TOTC20, which reads DO 10 I = 1, NM1, insert the following three cards:

```
      IF (K.GE.2)GO TO 8
      IF (ABS(TM1N(I,K)).LT. 0.001)TOTM(I) = 1.0
    8 CONTINUE
```

(ii) After card 16TOTC22, which reads DO 20 I = NL1, insert the following three cards:

```
      IF (K.GE.2)GO TO 18
      IF (ABS(TL1N(I,K).LT. 0.001)TOTL(I) = 1.0
   18 CONTINUE
```

All users of GEOCHEM should feel free to contact us about any problems they have with the program, or any new ideas for subroutines, or any new data, etc.

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